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NOTICES

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August, 1954

Number 2

DIRECT EFFECTS OF CLIMATE ON CATTLE

III. THE DIURNAL TREND IN BODY TEMPERATURE, RESPIRATION RATE AND PULSE RATE

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(Received for publication, 9 February 1954)

Summary

1. Three pairs of monozygotic twin Jersey heifers were housed in an indoor feeding barn for seven 24-hr. periods.

2. The results in the form of analyses of variance and graphs show that a distinct diurnal trend in body temperature and pulse rates takes place.

INTRODUCTION

Before any study can be made on the reactions of cattle to the direct effects of climate under New Zealand conditions it is necessary to know what variation occurs, under fairly normal air temperature conditions, with such factors as body temperature, respiration and pulse rates. One such source of variation is the diurnal trend. An experiment is described in this paper in which observations were made on the variation within a 24-hr. period of body temperature, pulse rate and respiration rate.

REVIEW OF LITERATURE

Kriss (1921), using two dry cows, observed their body temperatures by means of rectal thermometers every hour between 7.30 a.m. and 5.30 p.m. A rapid rise in body temperature occurred between 4 and 5 p.m. Defaecation had no effect, but drinking of water depressed body temperature for 2-3 hr., whilst food intake was found to increase the body temperature slightly for $\frac{1}{2}$ hr. afterwards. The highest body temperatures occurred in all cases in the afternoon, while the lowest was in the morning. He found no difference in body temperature when the cow was lying down or standing up.

Gaalaas (1945) analysed results of observations on body temperature and respiration rate of Jersey cattle. Regardless of the season of the year, the average body temperature and respiration rate per minute were considerably higher in the afternoon than in the morning. Manressa and Erce (1940) in the Phillipines found that the afternoon temperature of Jersey, Holstein and Indian Nellore cattle were significantly higher than the morning temperatures. The daily afternoon temperatures of the Jerseys were not significantly different from those of the Indian cattle, but those of Holsteins were different.

Duckworth and Rattray (1946) studied diurnal variations with Holstein-Zebu calves. They found that two maxima occurred in the body temperature readings, one at noon, and the other in the early evening. Differences in management had little effect in displacing these maxima. Minett and Sen (1945) took hourly observations for 24-hour periods on hill bulls and sheep and showed that the body temperature started to rise at 6 a.m., followed an upward trend to early evening, and then gradually fell to a minimum between 1 and 4 a.m.

Thus, there does appear to be a higher body temperature in the early evening in cattle and a lower body temperature in the early morning.

EXPERIMENTAL MATERIAL AND METHODS

Animals used

Three pairs of monozygotic rising-two-year-old Jersey heifers were used for this trial. For a fortnight before the commencement of the trial the animals were housed for increasing time intervals in an indoor feeding barn.

Feeding

While in the feeding barn the animals were fed pasture silage, and hay *ad lib*, plus 5 lb. of meal per day made up of linseed and coconut meal. Drinking water was available in automatic drinking cups and the animals were well bedded down with straw.

Recordings

The trial covered seven complete 24-hr. periods. For the first four periods readings were made every hour from 8 a.m. till 10 p.m. and then every two hours from 10 p.m. to 6 a.m. However, some variation was observed in body temperature according to whether the cows were lying down or standing. Therefore, in order to eliminate this possible discrepancy the readings were made every two hours during the last three 24-hr. periods, and all cows were made to stand at least 15 min. before a reading was made. Body temperature was measured with an ordinary clinical thermometer; pulse rates were determined by palpitation of the femoral or tibial artery; respiration rates were recorded by counting the flank movements.

Although it has been reported by Ritzman and Benedict (1938) that in the fasting steer or cow the energy expended in standing is about 9 per cent greater than in lying down and 12 per cent greater when the animal is fully fed, Kriss (1921) could find no difference in body temperature as between cows lying and standing. However, in this trial it was found that body temperature was higher when the cows were lying down than when the cows were standing. This is contrary to what

one would expect on the basis of Ritzman and Benedict's observation. A possible explanation is that when the cows were lying down their posterior regions were often sloping back into the drain running immediately behind them. This may perhaps have resulted in deep-seated abdominal organs which have a temperature which is normally higher than the rectal temperature being displayed towards the rear, with a resultant rise in the rectal temperatures.

RESULTS

Figs. 1-3 shows the graphs for body temperature, respiration rate and

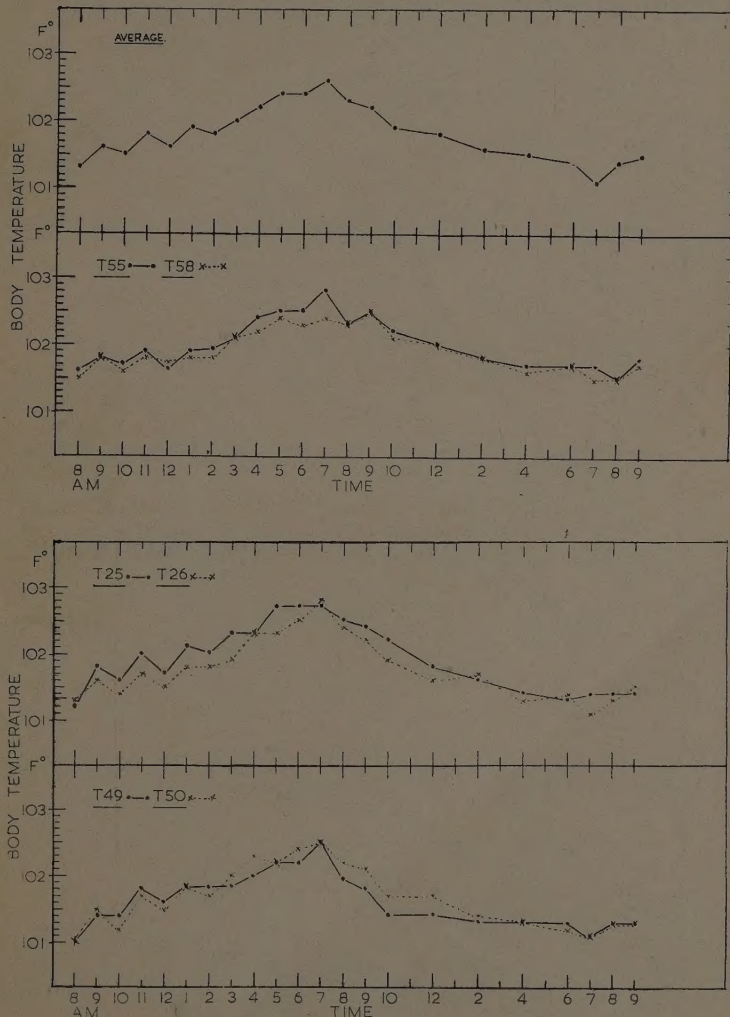


Fig. 1.—Graphs showing diurnal trends in body temperatures.

pulse rate. Each has a total graph which is an average for all cows and all periods. Then twin pairs are plotted together, each point being the average for the seven periods.

For the first four 24-hr. periods, measurements were made every hour during the day till 10 p.m. and then every 2 hr. till 6 a.m. The analyses of variance for this period are shown in Table 1.

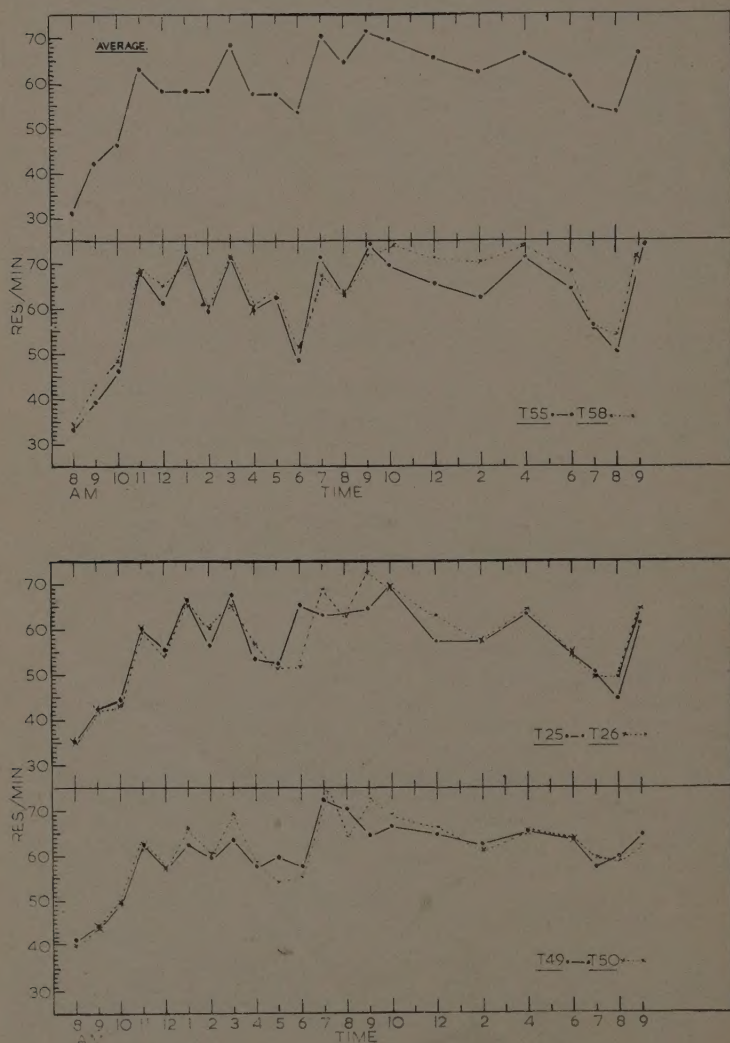


Fig. 2.—Graphs showing diurnal trends in respiration rates.

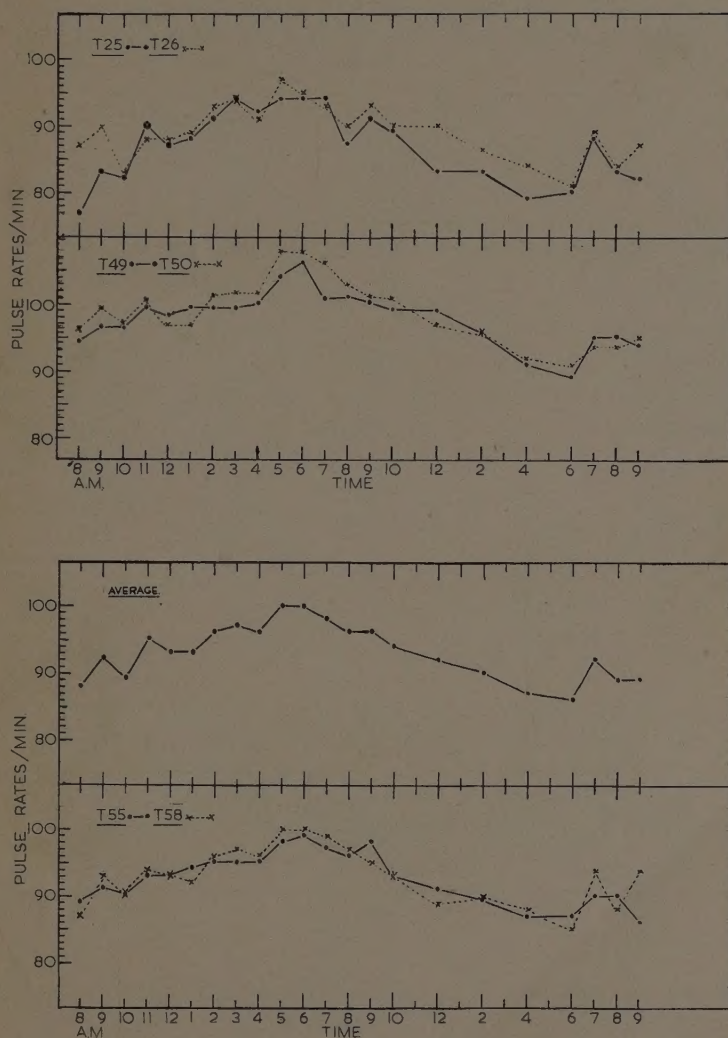


Fig. 3.—Graphs showing diurnal trends in pulse rates.

For Pulse rates in the above analysis the $D. \times A.$ interaction was highly significant, whereas $M. \times A.$ was non-significant. Therefore the $D. \times A.$ mean square was used to test differences between animals. For Respiration Rate and Body Temperature, both the $D. \times A.$ and $M. \times A.$ interactions are highly significant. In order to provide a valid test for animals, two adjustments must be made for each analysis

TABLE 1. ANALYSIS OF VARIANCE FOR: (a) BODY TEMPERATURE, (b) RESPIRATION RATE, AND (c) PULSE RATE

Source	d.f.	Body Temp.		Respiration Rate		Pulse Rate	
		M.S.	F.	M.S.	F.	M.S.	F.
Total	479						
Between Animals	5	1.76	*	771.40	**	1888.00	**
B. Twin Pairs	2	3.67	N.S.	1878.00	**	4605.00	**
Within Twin Pairs	3	0.48		33.66		76.60	
Between Days	3	2.26	**	9515.00	**	375.33	**
D. x A.	15	0.25	**	117.20	**	48.00	**
Day x T.P.	6	0.48	*	191.00	N.S.	68.16	N.S.
Day x W.T.P.	9	0.10		68.00		34.55	
B. Measurements	19	3.41	**	828.68	**	456.15	**
M. x A.	95	0.11	**	95.23	**	12.23	N.S.
M. x T.P.	38	0.17	**	182.62	**	19.11	**
M. x W.T.P.	57	0.06		37.37		7.64	
M. x D.	57	0.24	N.S.	227.31	**	46.89	**
M. x D. x A. (Error)	285	0.07		30.50		15.50	

N.S. = Not significant.

* = Significant at 5% level.

** = Significant at 1% level.

Accompanying statistics for the above analysis are shown in Table 2.

The standard deviation is derived in all cases from the appropriate error variance in Table 1.

TABLE 2. RANGE, MEAN, STANDARD DEVIATION AND COEFFICIENT OF VARIATION FOR BODY TEMPERATURE, RESPIRATION RATE AND PULSE RATE

	Body Temperature	Respiration Rate	Pulse Rate
Range	100.7—103.6° F.	28—102 per min.	72—117 per min.
Mean	101.9	64.85 per min.	93.67 per min.
S.	0.26	5.50	3.93
C	0.257%	8.48%	4.20%

by means of the method outlined by Wilm (1945). When the adjustments were made there was a highly significant difference between animals for both Body Temperature and Respiration Rate.

During the second session of the three 24-hr. periods, readings were taken every two hours. In Table 3 are found the analyses of variance for the three measurements.

TABLE 3. ANALYSIS OF VARIANCE FOR BODY TEMPERATURE, RESPIRATION RATE, AND PULSE RATE

Source	d.f.	Body Temperature		Respiration Rate		Pulse Rate	
		M.S.	F.	M.S.	F.	M.S.	F.
Total	215						
Between Animals	5	0.72	**	331.20	**	618.40	**
B. Twin Pairs	2	1.36	N.S.	765.00	**	1523.50	**
W. Twin Pairs	3	0.28		42.00		15.00	
Between Days	2	0.24	**	880.50	**	868.50	**
D. x A.	10	0.04	N.S.	52.10	N.S.	14.50	N.S.
D. x T.P.	4	0.03	N.S.	101.75	*	20.75	N.S.
D. x W.T.P.	6	0.70		19.00		10.33	
B. Measurements	11	2.52	**	1617.91	**	294.90	**
M. x A.	55	0.05	N.S.	48.63	N.S.	10.29	N.S.
M. x T.P.	22	0.06	N.S.	108.09	**	21.13	**
M. x W.T.P.	33	0.05		9.06		3.06	
M. x D.	22	0.06	N.S.	239.95	**	81.27	**
D. x M. x A. (Error)	110	0.05		35.82		8.84	

TABLE 4. RANGE, MEAN, STANDARD DEVIATION AND COEFFICIENT OF VARIATION FOR BODY TEMPERATURE, RESPIRATION RATE AND PULSE RATE

	Body Temperature	Respiration Rate	Pulse Rate
Range	100.7–102.7° F.	26–88 per min.	74–108 per min.
Mean	101.6	51.81	91.86
S.	0.22	5.98	2.97
C.	0.22%	11.54%	3.23%

Correlations were calculated on a within-cow basis for all possible combinations of the four variables, viz. air temperature, body temperature, respiration rate and pulse rate. The correlations for any two variables were tested by the method outlined by Snedecor (1948) to see whether they belong to a common population or not. It was found that only in the case of air temperature and respiration rate and air temperature and pulse rate was this the case, and an average correlation derived. For air temperature and respiration rate this was $r = 0.396^{**}$, and for air temperature and pulse rate, $r = 0.357^{**}$.

For the second section of the data, within-cow correlations showed high significance and all belonged to a common population as follows: air temperature and rectal temperature, $r = 0.256^{**}$; air temperature and pulse rate, $r = 0.333^{**}$; and rectal temperature and pulse rate, $r = 0.489^{**}$.

A difference was noted between body temperatures when the cow was lying down or standing up. On one day, body temperatures were taken with the cows that were lying down and then 15 minutes after they had been made to stand. The results are shown in Table 6.

Table 5 shows the range of air temperature experienced during each 24-hr. period.

TABLE 5. BODY TEMPERATURES OF COWS WHEN LYING DOWN AND WHEN STANDING

Twin No.	Lying (°F.)	Standing 15 min. (°F.)	Time
T 55	101.7	101.5	10 a.m.
58	101.3	101.3	
25	101.5	101.0	
26	101.4	101.2	
50	101.0	100.8	
49	101.2 (standing)	101.2	
55	101.8	101.5	12 p.m.
58	101.8	101.4	
25	101.8	101.9	
26	101.5	101.1	
50	101.6	101.3	
49	101.6	101.0	
25	101.9	101.6	2 p.m.
26	102.1	101.5	
50	101.6	101.4	
49	101.5	101.1	

TABLE 6. AIR TEMPERATURE RANGES FOR THE DIURNAL TRIAL

24-hr. period	Air temp. range (°F.)
1	47.0—67.0
2	55.0—68.0
3	55.1—72.0
4	51.2—70.3
5	52.8—59.0
6	46.2—61.0
7	51.9—57.5

DISCUSSION

In both analyses for body temperature a highly significant difference between animals was established. Twin pairs did not react together, though the number of animals left only a small number of degrees of freedom for testing between twin pairs. There was also a highly

significant difference between days and between measurements. That there should be a difference between measurements is obvious from the graphs. Days $\times$ animal and measurement $\times$ animal interactions were significant in the first analysis, but not in the second. During the first four days covered by the first analysis, cows which had been standing for some time had a lower body temperature than cows which were lying down; this may have brought about these significant interactions.

A highly significant difference between animals and between twin pairs was found for respiration rate. In both analyses, days and measurements were highly significant, which was to be expected because of the different air temperature conditions from day to day, and also within a 24-hr. period. Respiration rates were different in different animals at the same time however. It was noticed that when a cow was eating or had her attention distracted, her respiration was markedly lower than that of her twin sister which was just standing quietly. This would cause animals to vary in respiration rate at any one time regardless of air temperature. There was also a significant measurement $\times$ day interaction. Since respiration rates follow air temperature fairly closely it was to be expected that this interaction would be significant as air temperature at one time of measurement would not be the same every day.

A highly significant difference between animals, twin pairs, days, and measurements was found for the pulse rate data. The day $\times$ measurements interaction was significant in both analyses. Nervous upsets plus variation in feed intake at different times of the day could possibly account for this interaction. Although the measurements $\times$ animal interaction was non-significant in both analyses the twin-pair $\times$ measurement interaction was highly significant. This may be partly due to pulse rates being a strong characteristic of twin pairs and different twin pairs having different pulse rates at different measurements.

A feature of the pulse rates throughout his trial was the marked increase shown by the animals brought into the barn from outside. The range of pulse rates outside was 50-92; $\bar{x} = 70.23$; $s = 2.89$. Within the barn the range of 72-117; $\bar{x} = 93.67$; $s = 3.93$. The animals were very quiet and nervousness did not appear to be a factor over the whole period. The only factor which perhaps helps to explain the high pulse rates whilst inside the barn is the fact that in the barn the cows were fed to the limit of their appetite. It has been shown by Blaxter (1943) that pulse rates may increase by as much as 50 beats per minute during the course of a meal. He found that although all cows showed an increase in heart-beat rate during eating, some cows showed a greater response than others and it was not abnormal to find cows with pulse rates of over 100 per minute. The *ad lib* feeding conditions of this trial under which the cows could eat at frequent intervals throughout the day up till midnight may have caused the pulse rates to be quite high. There may not have been a sufficiently long interval between feeds for the pulse rate to fall to normal post-feeding level, before the cows started eating again. Pulse rates after midnight tended to fall almost to normal level in twin pair T25/T26 which ate very little during the early morning, but T49/T50,

being great foragers, ate more than the others during the period after midnight. This probably accounts for their high pulse rates.

There was a highly significant correlation between air temperature and respiration rate ($r = 0.396$) for the data covering the first four days. For the last three days there was virtually no correlation. During the last three days readings were taken every two hours. Usually the cows were lying down when the attendant walked into the shed. They were then all made to stand for a quarter of an hour before the first reading was taken. This disturbance of the cows and the resultant decrease in respiration rate may explain the lack of correlation during the last three days.

It is not clear why the correlation between air temperature and pulse rate should be higher and belong to a common population during the first four days but not for the last three days.

From the graphs, a distinct diurnal trend is evident both in body temperature and pulse rate. A peak always occurred at 5-6 p.m. and a minimum at 4-6 a.m.

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SOME EFFECTS OF SULPHUR AND PHOSPHORUS ON THE YIELD AND COMPOSITION OF RAPE (*Brassica napus*)

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(Received for publication, 8 June 1954)

Summary

Evidence is accumulating that sulphur deficiency may be important in some New Zealand soils. This paper presents a little more evidence that the gypsum contained in superphosphate may be of value in New Zealand agriculture, as in one trial rape responded significantly to gypsum in the presence of mono-calcium phosphate.

Chemical analysis of the rape and soils showed some interesting nutrient interactions and relationships.

INTRODUCTION

Sulphur has been referred to by Gilbert¹ as probably the most under-rated plant nutrient. As superphosphate is the main fertiliser used in New Zealand the significance of the gypsum it contains may not have been appreciated. In a soil rich in phosphate from previous applications, Sears² has noted responses from superphosphate on pasture growth which are almost certainly due to the sulphur contained in the fertiliser. More recent trials reported by Lobb³ in North Otago have shown responses on pastures, rape and lucerne, from applications of various forms of sulphur. Previous responses to both elemental sulphur and gypsum have been noted by Doak⁴ on lucerne, while Tennent and Duff⁵ noted responses on lucerne to the White Island product which contained 21.7% elemental S and 7.9% SO_3 . Earlier work by McConnell^{6, 7} with elemental S showed marked responses on swedes, rape and pasture. Recent work by Anderson⁸ has shown the importance of sulphur deficiency in several parts of Australia. It is of some considerable importance to assess the significance of sulphur in New Zealand agriculture, and trials have been initiated in Canterbury on rape and clover. Only the results of two rape trials are presented here, and outstanding effects of gypsum on the establishment and growth of clovers in the tussock country will be presented later.

EXPERIMENTAL PROCEDURE

The treatments were as follows:

1. Control (no treatment) (O)
2. Gypsum at 200 lb. per acre = 35 lb. S per acre (S)
3. Triple superphosphate (48% P_2O_5) at 200 lb. per acre (P)
= 96 lb. P_2O_5 per acre
4. 200 lb per acre each of gypsum and triple superphosphate
= 35 lb. S and 96 lb. P_2O_5 per acre (S + P)

The treatments were replicated four times and a Latin-square arrangement would have been ideal, but to simplify cultural operations the trials were put down as four randomised blocks in a long

strip. As ordinary superphosphate contains about 11.5% S the amount of gypsum applied corresponds to that contained in approximately 3 cwt. of superphosphate per acre. Triple superphosphate containing a negligible amount of sulphur was applied at a rate equivalent to approximately 4 cwt. of ordinary superphosphate (20% P_2O_5). The composition of the mixture applied in Treatment 4 is not therefore exactly the same as in ordinary superphosphate.

Individual plot size was 1/200th acre, and consisted of one drill-width (15 rows of rape), 8 yd. long. It is customary in New Zealand to drill reverted superphosphate in contact with the seed and the experimental area was drilled with $1\frac{1}{2}$ cwt. per acre ground limestone; as both soils were acid, this limestone should have served as an adequate source of calcium, if there were any danger of calcium deficiency. Also, it should offset any possibility that a response to gypsum was due to the calcium rather than the sulphate. The surrounding area was drilled with reverted superphosphate at $1\frac{1}{2}$ cwt. per acre, and though no additional lime was applied the crop was as good as on the best experimental plots and showed no sign of trouble associated with the acidity complex. In Trial 1, the fertilisers were broadcast by hand and lightly harrowed in before the seed was sown; in Trial 2, the seed was sown a few days before the fertilisers were applied, and accordingly they were not worked into the soil.

At harvest the middle four yards of the central seven rows in each plot were cut by hand to ground level, weighed in the field and sampled for dry matter and chemical determinations. Both soils were ploughed out of poor pasture, the fertilisers sown on 15 December, 1952, and the crops harvested on 27 February, 1953.

Soils and Climate

Both soils are on the Canterbury Plains near the foothills of the Southern Alps and in the genetic classification of New Zealand soils are placed in the category of intrazonal soils developed on gravel, occurring in the same area as the zonal Yellow Grey Earths. The parent material is greywacke alluvium and loess overlying the gravel of the river-fans. The shallowness of the soils overlying the gravel leads to droughty conditions in a normal summer; very free drainage and subsequent relatively intense leaching during the winter months, gives them their intrazonal character. The soil in Trial 1 is the Chertsey shallow silt loam, a typical profile being:

- 8 in. light brownish-grey sandy silt loam;
- 10 in. light brownish-yellow friable sandy silt loam *on* stones.

In Trial 2 the soil (known as the Lismore shallow silt loam), is similar but somewhat older, a typical profile being:

- 7 in. light grey-brown stony silt loam;
- 7 in. brownish-yellow stony silt loam *on* stones.

The soils are normally deficient in lime and phosphate, droughty, of poor structure and are used for mixed farming. The area selected for trials were chosen because of the higher rainfall near the foothills and the consequent greater leaching. The average annual rainfall is of the order of 30-40 in. but over the trial period was higher than average, and the normal summer drought was not operative during the period of the trial.

Analytical Methods and Soil Data

The method of Allison⁹ was used for organic carbon and that of Swanson and Latshaw¹⁰, using magnesium nitrate as oxidising agent, was adopted for total soil sulphur. Total sulphur in the plant material was determined by the method outlined in "Methods of Analysis, A.O.A.C."¹¹ and inorganic sulphur by the method of Johnson, Lindstrom and Gortner.¹² Standard procedures were followed for the remainder of the determinations. The soil data are presented in Table 1.

TABLE 1. SOIL ANALYSES

	Trial 1	Trial 2
pH	5.8	5.5
Citric soluble P_2O_5 * %	0.009	0.022
Truog P_2O_5 %	0.0012	0.005
Total N %	0.21	0.28
Carbon %	2.71	3.75
C/N Ratio	12.8	13.4
Total S %	0.035	0.046
N/S ratio	6.1	6.1

* 1:10 Ratio (Soil to 1% Citric acid) shaken 24hr. at 70°F.

"Available" phosphate was determined in the soil by the citric acid and Truog¹³ methods. The former method is used extensively by the Soil Bureau in New Zealand but it is recognised that it gives high figures on some soils, and in Trial 1, where phosphorus was extremely deficient in the field, the citric-acid-soluble phosphorus would have been classified as low. The phosphate status in Trial 2 would have been considered moderate. The Truog method is used in advisory work by the N.Z. Department of Agriculture and the particular system of classification used would have placed the soil in Trial 1 in the "deficient to very deficient" group, and that in Trial 2 in the "moderate to satisfactory" group, which agrees slightly better with the field responses.

RESULTS AND DISCUSSION

Yields of dry matter

In Table 2 are presented the yields of dry matter per acre with the statistical analysis of the results. Yields were low, but to some extent this was due to the very short period of growth. There was a very marked response to P in Trial 1, there being scarcely any crop in its absence. In the absence of S, P increased the yield of dry matter by 5 cwt. per acre, and in the presence of S, by about 7 cwt. per acre. The soil was so deficient in P that S had very little effect in the absence of P, but increased the yield by 2.4 cwt. per acre in the presence of P. In Trial 2, there were higher yields throughout, and whilst there was a

TABLE 2. YIELDS OF DRY MATTER IN CWT. PER ACRE

Treatment	O	S	P	S + P	Mean Yield	Main Effects		Interaction
						S	P	S × P
Trial 1	0.27	0.66	5.25	7.61	3.45	1.4**	6.0**	2.0*
Trial 2	12.2	15.1	16.6	15.6	14.9	0.9 n.s.	2.5*	-3.9 n.s.

n.s. = not significant

* = significant at the 5% level

** = significant at the 1% level

significant response to P, the response to S was just not significant. S increased the yields by 2.9 cwt. per acre without P and reduced the yields by 1 cwt. per acre with P. P was superior to no P by 4.4 cwt. per acre in the absence of S, and by 0.5 cwt. per acre when S was applied.

These trials provide added evidence that sulphur cannot be ignored in its effect on crop growth in New Zealand, and as Table 3 shows, the chemical composition of the rape throws further light on its effects.

The various treatments have not greatly affected the percentage of dry matter in the rape but there is a big difference between the two

TABLE 3. PERCENTAGE DRY MATTER AND COMPOSITION OF DRY MATTER OF RAPE

Treatment	Trial	O	S	P	S + P
% D.M.	1	12.2	12.1	11.2	11.3
	2	19.7	19.6	20.6	20.5
% N	1	5.33	4.11	2.89	2.24
	2	1.40	1.35	1.30	1.23
% Ca	1	3.34	3.48	2.51	2.27
	2	1.21	1.24	1.12	1.13
% P	1	0.12	0.13	0.23	0.25
	2	0.17	0.17	0.22	0.20
% Total S	1	0.58	0.89	0.50	0.78
	2	0.25	0.52	0.26	0.50
% Inorganic S	1	0.22	0.47	0.18	0.42
	2	0.09	0.31	0.10	0.29
% Organic S (by difference)	1	0.36	0.42	0.32	0.36
	2	0.16	0.21	0.16	0.21

trials. It was quite obvious at harvest that the rape in Trial 2 was much more mature than in Trial 1 and clearly suffering from nitrogen deficiency. This is reflected in the higher percentage of dry matter and the very low percentage of N in Trial 2 as compared with Trial 1. The increasing yields of dry matter as S, P, and S + P were applied in Trial 1, caused a marked reduction in the percentage of N but an over-all increase in the yield of N. In Trial 2 there was a slight fall in the percentage of N from an already low figure for the control, and very little difference in the total yield of N between the treatments. It is almost certain that the response to S, and perhaps P, in Trial 2 was limited by nitrogen deficiency, which is surprising in view of the reasonably good level of soil nitrogen. The crop was growing for only a very short time, however, and owing to the high rainfall, nitrate may have been heavily leached from the soils.

The effect of the treatments on the percentage of Ca parallels the effect on N, and there is clearly a close correlation between the N and Ca uptakes.

The percentage of P is very low in the no-P treatments in Trial 1, and where P was applied it has nearly doubled the percentage of P as well as greatly increasing the yield of dry matter. (See Table 2.) P has had a smaller effect in Trial 2 both on the percentage of P and yield of dry matter. The high Ca/P ratio is of interest, but as rape is normally used for fattening lambs in New Zealand it is probably of little nutritional significance.

The percentage of total S in Trial 1 was considerably higher than in Trial 2, but as in the case of N, owing to the higher dry matter yields the total uptake of S was greater in Trial 2. The application of S greatly increased the percentage of total S, mostly in the inorganic form, there being very little increase in the percentage of organic S. In data quoted by Miller,¹⁴ the percentage of total S of many different rape crops varied from 0.16 to 3.28, and the percentage organic S from 0.14 to 0.43.

After the plant's sulphur requirements have been met for protein and volatile-oil syntheses, it would appear that much of the absorbed sulphate accumulates in the inorganic form, in which state it may exert its effect on the molybdenum-copper balance in stock, as indicated by Dick.¹⁵

Uptake of Nutrients

It is of interest to compare the effect of the various treatments on the total uptake of the nutrients S, P, N and Ca. Among other things, such data permit a closer examination of the relationships between the nutrient status of different soils in a given region and nutrient uptake. In these experiments this is well demonstrated in the case of nitrogen. The percentage of N in the soil of Trial 2 was rather higher than in Centre 1, and there was approximately the same C/N ratio. The percentage of N in the rape of Trial 1 was considerably higher than in Trial 2, but owing to the higher yield of dry matter at Centre 2 the total yield was 24.2 lb. N per acre for the highest yielding treatment (P) and at Centre 1 was 19.1 lb. N per acre (S + P treatment). The ratio $\frac{\% \text{ N in Soil of Trial 2}}{\% \text{ N in Soil of Trial 1}}$ is 1.31, and the ratio of the yields of N at the two centres is 1.27. Evidence of this nature throws light on the

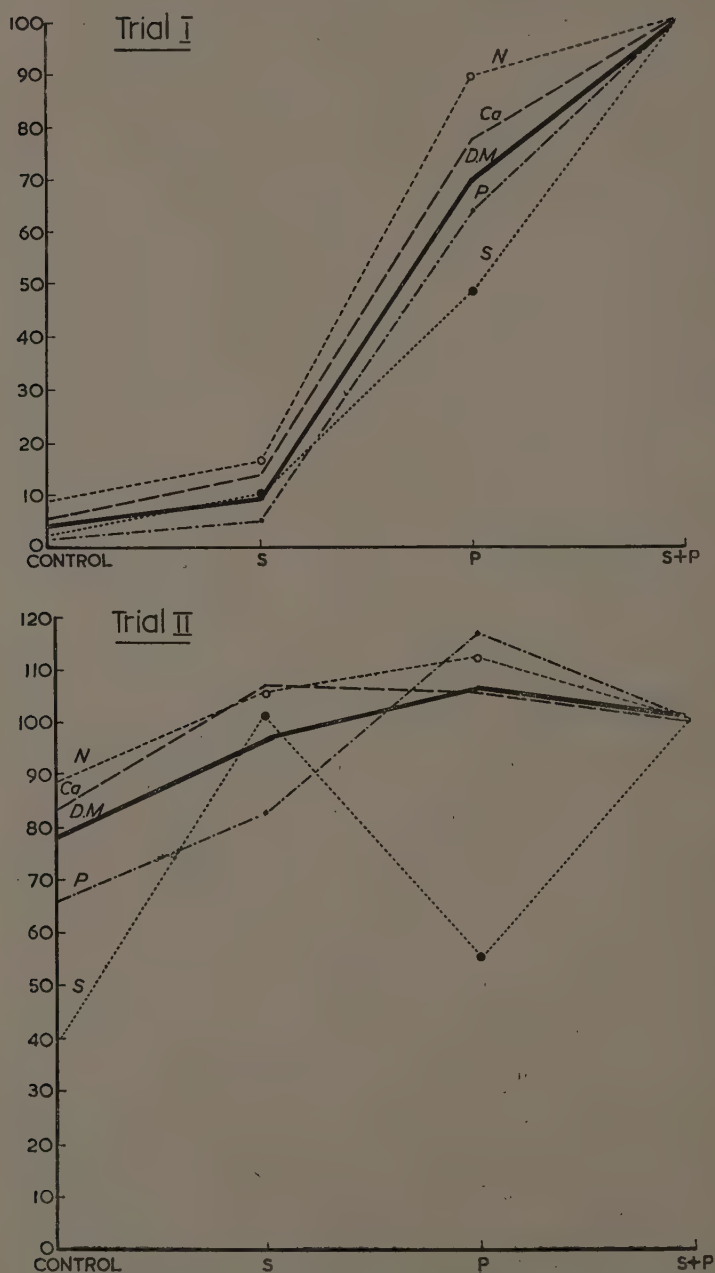


Fig. 1.—Yields of Dry Matter and nutrients as percentage of the yields for the S and P Treatments.

conflicting views on the value of soil nitrogen data for assessing the nitrogen nutrition of plants. Once any serious deficiencies of other nutrients have been made good, the uptake of N from soils in a given region in the absence of applied N may be closely correlated with the total soil nitrogen. Yields of dry matter alone may often be of little value for comparing nutrient levels in different soils.

The N/S ratios in the two soils are the same (6.1) and American evidence¹⁶ suggests a direct correlation between the total organic sulphur and amounts of nitrogen and carbon, particularly in chernozems and black prairie soils and, to a lesser extent, in podzolic soils. The total-N : total-S ratios were on the average 6.4 for chernozems, 6.1 for black prairie soils and approximately 8 for podzols. Both the percentage of N and percentage of S in the A horizon of the two soils under trial would give them affinities with the black prairie soils rather than the podzols, and their N/S ratios are identical with the American average for black prairie soils.

The ratio between the percentage total S of the two trial soils is 1.31. In comparing the total S uptake by the plants with the soil S it is essential to exclude the S-treated plots, and the ratio of the S uptakes on the P-treated plots is 1.64. This higher ratio may be due to the fact that S was more deficient in Trial 1 than Trial 2, or perhaps the amount of phosphate applied in Trial 1 was still inadequate to give maximum dry matter increase and higher yields of S.

A convenient and illuminating method of expressing yield data for nutrients is indicated in Fig. 1.

The yields of dry matter and nutrients for the various treatments are calculated as a percentage of yields for the S + P treatments. The application of S in Trial 1 has given a slightly higher yield of dry matter, and corresponding increases in N, Ca and S relatively greater than the increase in dry matter, whereas the increase in yield of P which was extremely deficient in this soil is relatively less than that of dry matter. The P treatment gave parallel increases in yield of D.M., N, Ca and P, but a relatively smaller yield of S. A deficiency of S cannot really be assumed, because the S + P treatment may have caused luxury consumption of S, and the percentage yield of S for the P treatment could be low on that account.

In Trial 2, the S treatment increased the yield of dry matter with parallel increases in the yields of N, Ca and P, and a bigger relative increase in the yield of S. P gave the highest yield of dry matter with parallel increases in the yields of N, Ca and S over the control treatment, whereas the S + P treatment gave a lower yield of dry matter and a lower percentage N and P than the P treatment. It is possible in this case that the sulphate ion supplied in the gypsum reduced both the uptake of the phosphate and the nitrate ion, and the obvious deficiency of nitrogen in this trial, may have caused the reduction in yield of dry matter. The position may have been quite different at a high level of N nutrition. Care must be taken in the interpretation of such data for fertiliser trials, particularly if treatment differences in dry matter yields are not significant.

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HORMONAL INDUCTION OF LACTATION IN IDENTICAL-TWIN DAIRY CATTLE

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Summary

An experiment is reported in which both growth of the udder and lactation was induced experimentally in seven heifers, the success of the experiment being measured by comparing the extent of lactation with that following normal pregnancy in the identical twin mates of the experimental animals.

The growth of the udder was stimulated with oestrogen (diethylstilbestrol) and progesterone administered during a period of five months in which the two hormones were injected in a ratio of 1 μ g. of diethylstilbestrol to 1 mg. of progesterone (ratio 1:1000 parts by weight). These hormones were injected in increasing amounts starting with 50 mg. of progesterone daily for two months, 75 mg. for the third month, and 100 mg. daily for the final two months.

Lactation was initiated by the administration of increased amounts of diethylstilbestrol during the final 30-day period. For the first 10 days, 2 mg. was injected, followed by 4 mg. and 8 mg. for the final 10 days. Twice-daily milking was started at the time the normal mate calved.

Three of the seven sets of twins were very low producers. Their experimental milk production was 10.8, 83.7 and 106.9 per cent of the normal lactation. The other four animals produced 41.9, 49.1, 61.1 and 72.5 per cent of the milk (FCM) of the normal mate.

INTRODUCTION

Throughout New Zealand, sterility in dairy cattle is a major cause of herd wastage. Ten per cent of all yearling heifers and 7.4 per cent of mature cows fail to conceive during the three months of spring mating. Though approximately 80 per cent of these animals¹ will conceive subsequently if given the chance, such out-of-season breeding is uneconomic and the animals concerned are usually culled from the herds. It is apparent, therefore, that any technique capable of reducing the incidence of temporary and permanent sterility, or, alternatively, of bringing these sterile animals into lactation, is one that has considerable practical possibilities.

Some years ago a number of workers found that lactation could be induced in non-parturient goats by the administration of oestrogens. Since that time, numerous experiments have been carried out in many countries, employing both goats and cows and administering various oestrogenic substances (both synthetic and natural)^{2 3 4}. Almost invariably these studies have indicated that the milk yields obtained from animals brought into lactation in this manner were usually far less than might be expected from normal parturient lactating animals, and further, that the lactational response of similar animals to identical treatments was most variable.

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Experience accumulated from numerous experiments has led many workers to the belief that both oestrogen and progesterone therapy are required in most species in order to produce mammary growth comparable to that of mid-term pregnancy, as both lactational response and histological structure appear more normal with this combination therapy than is the case when oestrogen alone is used. However, a serious handicap to techniques of inducing non-parturient lactation has been the lack of knowledge concerning the endogenous secretion rate, and blood level of the hormonal factors involved in mammary development.

In dairy cattle, the amount of oestrogen excreted in the urine has been shown to rise gradually with the advance of pregnancy⁵, while it has been shown to be high in the faeces prior to parturition⁶. By the technique of removal of the ovaries or corpora lutea of goats and cattle in early pregnancy and the determination of the amount of progesterone required to maintain pregnancy, an estimate of the endogenous secretion of progesterone has been made. In goats the progesterone requirement has been shown to be of the order of 10 to 15 mg. daily⁷. In dairy cattle the estimates are of the order of 100 mg. daily⁸.

A second problem is the best synergistic relation between oestrogen and progesterone for optimal mammary gland growth. It is suggested that the ratios of oestrogen to progesterone ranging from one part of oestrogen to 10-100 parts of progesterone which have been used in the past are too narrow. Recent work indicates that ratios of 1:1000 or more are more satisfactory in the case of dogs⁹, rats¹⁰ and mice¹¹. In studies on the induction of lactation in goats, it has been shown that the lobule-alveolar system appears more nearly normal as the ratio of oestrogen to progesterone has been widened³.

While much more basic data is needed as to the amount of oestrogen and progesterone circulating in the blood of the cow during pregnancy, the above estimates furnish a starting point for a study of the value of hormone therapy in inducing growth of the udder and lactation in non-parturient heifers.

The use of identical twins in such studies is especially important in evaluating the results of hormone therapy since genetic differences in cattle and goats are very great. In this experiment, one of a set of twins was bred and the post-parturient lactation was compared with its mate in which udder growth and lactation was induced by hormone treatment.

It should be pointed out that two problems are involved in such studies. The first problem is to stimulate the growth of the heifer's udder similar to that which takes place during the first half to two-thirds of pregnancy¹². This will be accomplished, it is believed, when amounts of oestrogen and progesterone in the proper total amount and in the correct ratio of the two are administered during a corresponding period of time.

The second problem is to stimulate the secretion of milk in the udder thus grown. For this purpose, prolactin has been shown to be effective in many experimental animals². However, this material is not readily available. A second alternative is to stimulate the secretion of endogenous lactogenic hormone at a time when the growth phase is

completed. It has been suggested¹³ that this is accomplished in normal pregnancy in cattle by an increase in the endogenous secretion of oestrogen which overrides, physiologically, the action of progesterone, thus also initiating the processes which lead to parturition.

EXPERIMENTAL PROCEDURE

Animals

Seven sets of identical twin (grade Jersey) heifers were used. These sets were split such that a comparison was obtained between the production of normally calving twins and their mates in which both mammary growth and lactation were induced by hormone therapy.

Hormone-therapy growth phase

Diethylstilbestrol was used as the source of oestrogen stimulation. Crystalline progesterone was used as the source of luteal stimulation. The ratio of these two substances on a gravimetric basis was 1:1000, i.e., each microgram ($\mu\text{g.}$) of diethylstilbestrol was injected with one milligram (mg.) of progesterone. These hormones were dissolved in peanut oil and administered together daily by subcutaneous injection.

The diethylstilbestrol—progesterone daily therapy was as follows:

- Period 1: 60 days, 50 mg. progesterone : 50 $\mu\text{g.}$ diethylstilbestrol.
- Period 2: 30 days, 75 mg. progesterone : 75 $\mu\text{g.}$ diethylstilbestrol.
- Period 3: 60 days, 100 mg. progesterone : 100 $\mu\text{g.}$ diethylstilbestrol.

Hormone-therapy lactation initiation phase

To induce the initiation of lactation in the udder developed by the above hormone treatment, the injection of additional amounts of diethylstilbestrol was begun during the last 30 days of Period 3 above. The rate of injection was 2 mg. per day, for 10 days, then increased to 4 mg. per day for 10 days, and then increased to 8 mg. per day for the final 10 days or until the animal's co-twin calved, at which time regular milking was commenced.

Production records

All heifers were milked twice daily under standardised milking conditions. Milk yields were recorded twice daily and a composite of the morning and evening samples was tested daily for fat content. A detailed analysis of milk composition was carried out each fortnight. These latter data will be reported elsewhere by D. D. Perrin (Pers. Comm.).

RESULTS

Of the seven pairs of twin heifers, only four pairs produced approximately normal amounts of milk and fat. Details of the yield and persistency of each animal are shown in Table 1. Fig. 1 presents the lactation curves of milk and fat for the four animals that registered "normal" production yields.

TABLE 1. COMPARISON OF THE MILK PRODUCTION OF NORMAL AND EXPERIMENTALLY INDUCED LACTATION IN PAIRS OF IDENTICAL TWINS

Twin No.	Treatment*	Days in Milk	Total Milk (lb.)	Total Fat (lb.)	Fat (%)	F.C.M. (lb.)	Yield of Treated Animals as % of Normal (F.C.M. Basis)
T241	E.P.	259	3288	161	4.90	3730.2	49.08
T242	N	305	7113	317	4.46	7600.0	
T258	E.P.	153	624	27	4.33	654.6	83.70
T257	N	170	755	32	4.24	782.0	
T262	E.P.	262	2034	106	5.21	2403.6	41.94
T261	N	262	5026	248	4.93	5730.4	
T268	E.P.	288	4091	182	4.45	4366.4	61.13
T267	N	305	7394	279	3.77	7142.6	
T276	E.P.	280	3143	147	4.68	3462.2	72.48
T275	N	280	4441	200	4.51	4776.4	
T277	E.P.	85	482	23	4.77	537.8	106.87
T278	N	85	433	22	5.08	503.2	
T284	E.P.	41	69	2	2.90	57.6	10.77
T283	N	95	587	20	3.41	534.8	

* N = normal lactation.

E.P. = oestrogen- and progesterone-induced udder growth and lactation.

Of the four sets which secreted "normal" amounts of milk and fat, the non-parturient lactating members were stimulated to secrete from about 42 to 72 per cent as much as the control mates. It is interesting to note that the average percentage of fat in the milk showed an increase in every animal in which non-parturient lactation was induced. In two of the four pairs, the duration of lactation was the same, whereas in the other two pairs the experimentally stimulated lactation was shorter.

A close similarity in ranking order between the yields of the experimentally induced lactations and those of the co-twins is apparent, illustrating in effect a relationship between the yield of the non-parturient animal in which lactation has been hormonally induced and the normal lactation potential of the same animal.

The reason for the very low yields of three sets is not at all clear. It is apparent, however, that in these sets the failure of lactation cannot be attributed to a deficiency of the gonad hormones.

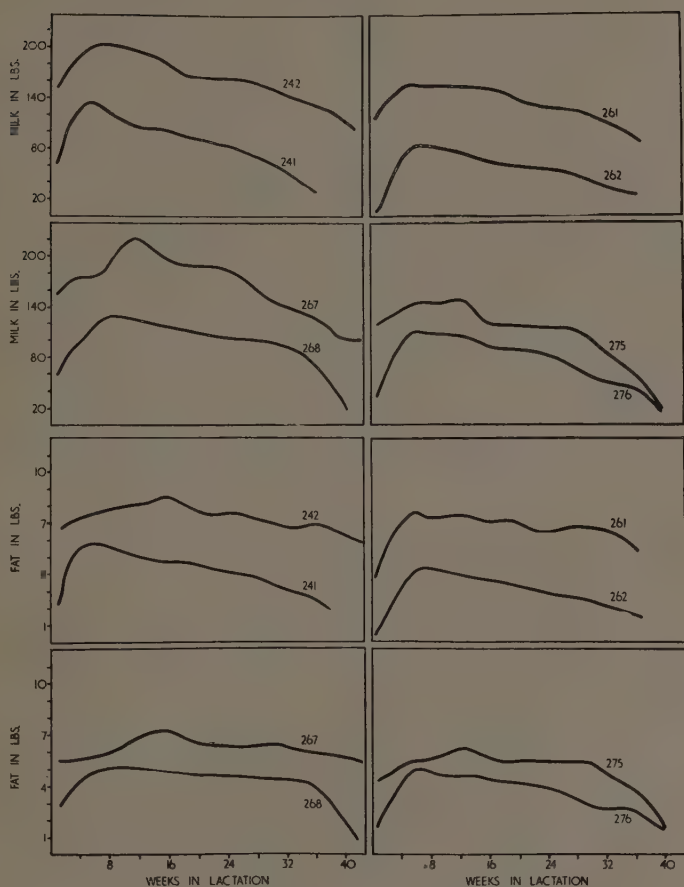


Fig. 1.—Lactation Curves for Milk and Fat.

DISCUSSION

The present experiment is the first to be reported in which identical twin cattle have been used to measure the extent of lactation that can be stimulated, without pregnancy, by means of the gonad hormones, oestrogen and progesterone. These animals are ideal for such experiments as it has been shown that identical twins which calve normally and are fed alike usually produce very similar amounts of milk and fat¹⁴. Moreover, this experiment illustrates the necessity of using control animals identical in genotype with those subject to the hormonal induction of lactation if a valid measure of the efficiency of the therapy treatment is to be obtained. Experiments conducted with the object of measuring the relative efficiency of various hormone treatments in inducing lactation must be interpreted in the light of this observation.

Unfortunately, it did not prove possible to measure, independently, the success of the endocrine therapy in regard to the completeness of udder growth, as compared to the success in stimulating the secretion of the lactogenic hormone.

Although the production of the animals brought into lactation by hormone therapy was appreciably less than that of their normal parturient mates, considerable amounts of milk were actually secreted by the experimental animals, sufficient indeed to bring the technique of the induction of non-parturient lactation into the realm of practical possibility. Certainly, it is not too much to expect that a hormone therapy programme can be developed which will stimulate growth of the udder and the secretion of milk equal to that of normal animals.

A useful index of success in such experiments would seem to be the comparison of milk and fat production at the period of maximum production, i.e. within the early months of lactation. The rate of decline and persistency of milk secretion probably involves the problem of the continued secretion of lactogenic hormone, thyrotropic hormone, and growth hormone. The influence of thyrotropin and growth hormone on the lactation yield of identical twins will be reported separately. Whether these other pituitary hormones are influenced by oestrogen administration in a similar manner to the stimulation of lactogen is not at present known.

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SEED VARIATION IN PEA ROGUES

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Summary

While rogue plants do not differ from normal plants in seed yield, they differ significantly in seed numbers and single seed weight. Low seed weight is associated with high number. Differences in these characters occur to a lesser degree between rogue lines and between normal lines.

Differences in single seed weight among four lines of normal peas and four of rogue over two generations suggest that these differences are heritable.

INTRODUCTION

Bateson and Pellew (1915), in reporting the occurrence and preliminary genetic study of the "rabbit-eared" rogue in several varieties of garden peas, stated that the seeds of this rogue were, on the average, smaller than those of the normal type plant. It seemed as though this fact might be connected with the general observation of seedsmen and growers that pure stocks of seed of varieties prone to producing this rogue, tend to "run back": that with successive generations where roguing is not practised or is not effective, the proportion of rogues increases. If smaller seed is associated with equivalent yield of plant, then the resulting increased fecundity could partly account for this increase.

Of the garden peas grown for seed in New Zealand, the most important variety producing "rabbit-eared" rogues is Onward. Pure seed grown by the Crop Research Division by single plant selection for varietal trueness produces rogues, and these occur spontaneously from the first single plant progeny to subsequent generations. The numbers thus occurring, however, do not compare with those found in unrogued or ineffectually rogued stocks. It is on this material, then, that the present investigation on seed characters is based.

MATERIAL AND METHODS

In 1950 a seed merchant's sample of Onward peas derived from pure seed in 1948, was grown at the Crop Research Division. From it, four rogue plants and three normal plants were selected, together with one normal plant from the Division's pure seed area. These were designated R1-R4 (rogue) and N1-N4 (normal), and harvested separately to be grown in the season 1951/52. After the next harvest, each line was weighed, the average weight per seed being the index of seed size. In the season 1952/53, all the seed from the eight lines was sown in a randomised block trial of fifteen replications. Each plot was a single row of eight seeds spaced six inches apart. Plots were two feet apart. The plants were harvested individually, and for each plant the weight and number of seeds were recorded, and the average weight of one seed calculated. Seed-weight distribution graphs in each line were prepared from weighings of all available seed singly in 1951/52, and from samples of two hundred seeds per line in 1952/53.

Diseased plants were discarded from the trial, as were plants producing less than ten seeds, and the few cracked seeds were excluded. Throughout the trial, plants were observed for trueness to type, i.e. whether rogue or normal. No aberrations were recorded.

RESULTS

Seed Differences between Rogue and Normal Peas

In Table 1 the seed yield per plant, seed numbers per plant and the average single seed weights of the eight lines of rogue and normal types over the 1952/53 trial are given (Columns 1, 2, 3). Although the

TABLE 1. COMPARISON OF YIELD PER PLANT, NUMBER OF SEED PER PLANT AND SEED WEIGHT IN ROGUE AND NORMAL ONWARD PEAS

Line No.	Seed Yield 1952/53 Mean yield per plant (g.)	Seed Numbers 1952/53 Mean No. seed per plant	Seed Weight 1952/53 Mean wt. per seed (g.)	Seed Weight 1951/52 Mean wt. per seed (g.)
N1	13.9	43.3	0.325	0.322
N2	14.6	45.2	0.322	0.337
N3	14.0	41.1	0.340	0.361
N4	11.9	35.8	0.331	0.350
	Group Mean 13.6	Group Mean 41.4	Group Mean 0.330	Group Mean 0.343
R1	15.7	54.2	0.288	0.304
R2	13.3	47.5	0.289	0.306
R3	14.7	54.1	0.272	0.290
R4	16.1	57.7	0.274	0.262
	Group Mean 15.0	Group Mean 53.4	Group Mean 0.281	Group Mean 0.291
Significant Difference between N & R Means at 5% level of significance = 2.10		Sign. Diff. between N & R Means at 5% level of sign. = 7.20	Sign. Diff. between N & R Means at 5% level of sign. = 0.015	Sign. Diff. between N & R Means at 5% level of sign. = 0.032

mean yield per plant of the four rogue (R) lines exceeds that of the four normal, the difference is not significant. However, in the gross yield components, seed weight and seed number, significant differences are shown. Low seed weight in rogue plants is compensated by high seed number to produce a total yield per plant approximating that of the normal type.

Seed Differences within Rogue and Normal Peas

The analyses of variance plotwise of seed yield per plant, seed number per plant, and weight of single seed (Table 2 and 3) of normal

and rogue lines show that within each type, numbers of seeds per plant and single seed weight are significantly different. Yield differences are non-significant.

TABLE 2. ANALYSES OF VARIANCE OF YIELD, NUMBERS AND WEIGHT OF SEED IN FOUR NORMAL LINES OF ONWARD PEAS, GROWN 1952/53.

Source of Variance	d.f.	Mean Squares		
		Yield	Numbers	Weight
Total	59			
Replications	14	5396**	46923**	201
Lines	3	2155	24493*	931*
Error	42	863	7439	250

*F exceeds 5% level of significance.

**F exceeds 1% level of significance.

TABLE 3. ANALYSES OF VARIANCE OF YIELD, NUMBERS AND WEIGHT OF SEED IN FOUR ROGUE LINES OF ONWARD PEAS GROWN 1952/53

Source of Variance	d.f.	Mean Squares		
		Yield	Numbers	Weight
Total	59			
Replications	14	5849**	76895**	113
Lines	3	2204	26991*	1274**
Error	42	936	8582	107

*F exceeds 5% level of significance.

**F exceeds 1% level of significance.

Seed Weight

The data for mean single seed weight given in Table 1 (Columns 3 and 4) of each line for two successive generations, together with the demonstration of statistical significance of differences in the second generation (Tables 2 and 3), strongly suggest a similar situation to that in French beans (Bateman, 1952), where variation in ten-bean weight within a strain was reported. In the present experiment, all lines with the exception of N4, were selected from within a single strain of known origin, and the progeny of lines from the 1951/52 season showed a consistent relative order in the next season, with the exception of R3 and R4. Fig. 1 shows the distribution for single seed weights for two years in N2 and N4, R2 and R3.

The constant difference in mean weight per seed between N and R groups is notable (Table 1, Columns 3 and 4). In the first year the difference was 0.052g., and in the second, 0.049g.

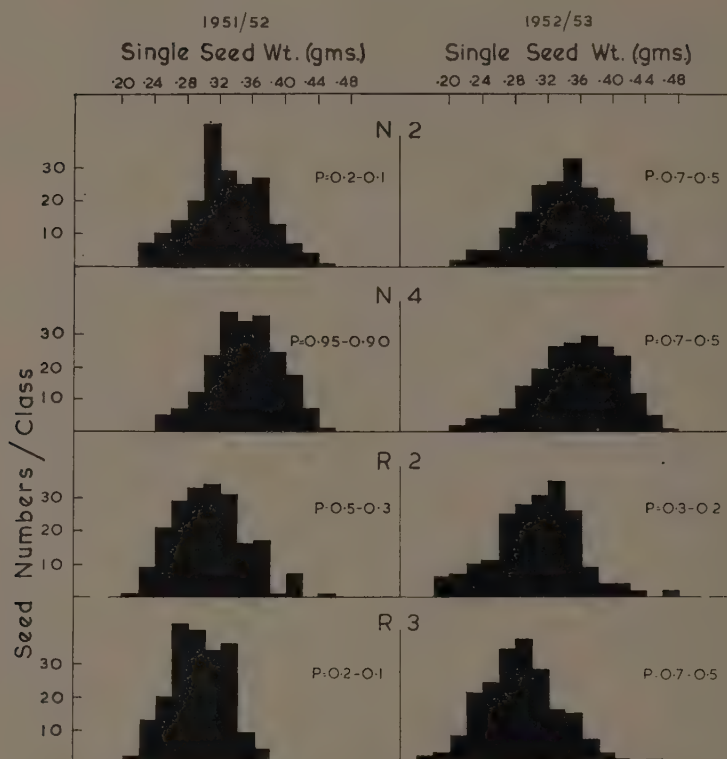


Fig. 1.—Distribution of single-seed weights in normal and rogue peas.

DISCUSSION

The rapid increase in numbers of "rabbit-eared" rogues in merchant's strains of Onward peas seems to be explained in this experiment. Four selections of rogues average nearly 30% more seeds per plant than the four normal selections. The competitive effects of growing under field conditions are unlikely to erase this difference.

The lowered mean seed weight in the rogue lines suggests an additional effect of the rogue character on the expression of genes for seed weight (Tschermak, 1912). Rogues cannot be recognised by their individual seed weights as the distribution graphs show, but by the average weight of a line. The variation within lines of both normal and rogue types strongly resembles that in the wheat cross material of Palmer (1952) where selection for kernel weight, while effective, had no effect on total yield owing to a negative correlation with the number of kernels per plant.

The indication of heritable differences in seed weight in strains of Onward peas, both normal and rogue, demonstrates again the occurrence of distinct pure lines within a commercial strain, as first shown by

Johannsen (1903, 1909). Selection, firstly through the Crop Research Division's single plant selections to form nucleus seed, and then by merchants, has not made the variety uniform.

The direct source of the rogue lines in this experiment is not known. As they were not selected from separate pure lines of normals, it is not known whether the lower seed weight lines of rogue are derived from low seed weight lines of normal, or whether the rogue "mutation" is itself variable. If the latter is not so, it should be possible to estimate the quantitative effect of the rogue condition on seed weight by the selection of rogues in pure lines of peas.

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RESISTANCE OF SWEDE VARIETIES TO DRY-ROT (*Phoma lingam* (Tode) Desm.)

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Summary

1. Dry rot (*Phoma lingam* (Tode.) Desm.) is a serious and widespread disease of swedes (*Brassica napo brassica* Mill.) and turnips (*B. rapa* L.) in South Otago and Southland.
2. The incidence of severe dry rot in crops of the swede variety New Zealand Wilhelmsburger is low.
3. An inoculation technique which gives uniform infection in susceptible varieties is described.
4. Forty-five lines of swedes were tested for reaction to dry-rot in glass-house and field trials. Many of the varieties appeared to be mixtures of susceptible and resistant plants. The varieties Weibull's Balder, Weibull's Wilhelmsburger, and a line of Wilhelmsburger Otofte of unknown origin, had a high proportion of resistant plants.

INTRODUCTION

Dry rot of swedes was first recorded in New Zealand by Kirk (1905). Several investigations of the biology of this disease have since been reported (Cunningham, 1927; Neill, 1929; Cottier, 1930; Hughes, 1933; Gibbs and Brien, 1935; and Dennis, 1941.). These authors have shown that the disease can be carried over in the soil or in the seed; that it can persist between seasons on weed hosts; and that it can be spread by insects. Unpublished tests have shown that the incidence of the disease in seed sown in New Zealand is now very low, but dry rot still causes severe annual losses.

TABLE 1. PREVIOUSLY REPORTED RESISTANCE TO DRY-ROT IN SWEDE VARIETIES

Variety	Author	Country
Wilhelmsburger Studsgaard Bangholm	} Anon., 1929	Denmark
Incomparable Greentop Keepwell Magnum Bonum	} Murphy, 1927	Ireland
Studsgaard Herning	} Whitehead and } Jones, 1929	Wales
Garton's White Fleshed Conqueror	} Whitehead, 1940	Wales
New Zealand Wilhelmsburger New Zealand Sensation Calder	} Hadfield, 1952	New Zealand

* Stationed at Crop Research Division.

Several authors have reported varietal differences in resistance to dry rot: viz. Levy (1920), Murphy (1927), Whitehead and Jones (1929), Dennis (1939), Whitehead (1940), and Hadfield (1952). Varieties which have been described as resistant are listed in Table 1.

This report indicates the present incidence of dry-rot in New Zealand, and records the incidence and severity of the disease on different varieties following artificial inoculation.

DISEASE SURVEY

Surveys to determine the incidence of dry-rot and club-root (*Plasmodiophora brassicae* Wor.) in swede and turnip crops in South Otago and Southland were made in winter (June) from 1950 to 1952. Over half the New Zealand acreage of swedes and about one fifth of the turnip area is grown in these districts. In each crop the incidence of diseased plants was listed as trace (less than 1% of plants infected), slight (1 to 10% of plants infected), moderate (10 to 30% of plants infected), or severe.

Results of the three surveys are listed in Table 2.

TABLE 2. INCIDENCE OF DISEASE IN SWEDE AND TURNIP CROPS IN SOUTH OTAGO AND SOUTHLAND

Year	Disease	Percentage of Crops Infected					Number of Crops
		Severe	Moderate	Slight	Trace	Total	
1950	Dry Rot	11.6	18.8	34.8	30.4	95.6	69
	Club-root	10.1	4.4	17.4	26.1	58.0	
1951	Dry Rot	8.1	9.2	35.6	29.9	82.8	87
	Club-root	11.5	4.6	19.6	24.1	59.8	
1952	Dry Rot	8.0	22.0	33.0	28.0	91.0	100
	Club-root	4.0	4.0	12.0	4.0	24.0	

Dry rot was much more common than club-root, and caused greater losses. The percentage of crops in each grade was reasonably consistent from year to year.

The distribution of infection classes among the different varieties seen during the surveys is shown in Table 3.

TABLE 3. DISTRIBUTION OF DRY-ROT INFECTION CLASSES AMONG SWEDE VARIETIES OVER THREE SURVEYS

Variety	Percentage of Crops in each Class				Number of Crops
	Severe	Moderate	Slight	Trace	
Grandmaster	22	29	32	17	41
Superlative	5	32	39	24	59
Crimson King	6	11	56	28	36
N.Z. Wilhelmsburger	0	0	20	80	35
N.Z. Sensation	33	0	17	50	6
Calder	8	23	23	46	13
TOTAL	9	20	35	36	190*

* Balance of crops were turnip varieties.

In no crops of New Zealand Wilhelmsburger was the incidence of disease rated as severe or moderate, but some crops of all other varieties were in one or other of these categories.

EXPERIMENTAL METHODS

A series of trials was conducted to determine the relative resistance of varieties to dry-rot, and to provide resistant plants for breeding.

Most investigators of varietal resistance to dry-rot have relied on the natural occurrence of the disease. Seed-born infection may, however, vitiate the varietal comparisons which have been drawn from such trials. In the trials reported here, all ~~bulbs~~ ¹⁰⁰⁰ were artificially inoculated.

P. lingam (Type II b, Cunningham 1927) was cultured on sterilised whole pea seed (see Cruickshank, 1953). Profusely sporulating cultures were shaken with sterile water, and the suspension from one 250-ml. culture flask was diluted to give one litre of spore suspension.

The upper part of each bulb was inoculated just below the cortex with this suspension, using a continuous flow hypodermic syringe with a 24 gauge needle.

Forty-one varieties were tested in two trials in the glasshouse at Lincoln, and forty-five varieties in field trials at Lincoln and Palmerston North. In each glasshouse trial, 17 bulbs of most varieties were injected with spore suspension, and one with sterile water.

The field trials were arranged as a simple lattice, with four replications at Lincoln and two at Palmerston North. The number of plants per plot varied from 0 to 40, but only four plots contained no plants (two plots of Variety 34 and one of 33 at Lincoln, and one of Variety 34 at Palmerston North).

Results were recorded eight weeks after inoculation, roots being graded into the following categories:

- | | |
|---|-------------------|
| 0. lesion corked over at injection site—no pycnidia | |
| 1. lesion less than 1 cm. diam.— | few pycnidia |
| 2. lesion more than 3 cm. diam.— | few pycnidia |
| 3. lesion more than 3 cm. diam.— | abundant pycnidia |
| 4. large lesion— | plant dead. |

RESULTS

Bulbs injected with sterile water did not become infected with dry-rot, and all were scored type "O".

At the outset, no varieties were known to be completely resistant, though some were thought to be completely susceptible. It is therefore necessary to examine the reliability of the test before considering varietal differences.

From the plant breeder's point of view, a test in which varieties known to be susceptible failed to develop the disease would be suspect,

but would in fact be more useful than one in which all plants succumbed. In the former case, field tests would eventually show any errors; in the latter, no material would be available for field test.

Mean scores in the three trials are presented in Table 4.

TABLE 4. MEAN SCORES OF DRY-ROT INFECTION OF SWEDE VARIETIES

No.	Variety	Glasshouse Trials	Field Trials		Both
			Lincoln	Palmerston	
1	Aberdeen Prize Purple Top	2.3	2.85	2.80	2.83
2	" " " "	2.1	2.87	2.95	2.90
3	Bangholm Wilby Otofte	2.2	2.85	3.00	2.93
4	" Otofte	2.5	2.97	2.95	2.97
5	" Pajberg	2.4	2.95	2.95	2.95
6	" Hinderupgaard	2.5	2.80	3.00	2.87
7	Cullen's May Day	2.6	2.95	3.00	2.97
8	" Best of All	2.5	3.00	2.90	2.97
9	Dunn's Defiance Purple Top	2.6	3.00	3.00	3.00
10	D.S. 32	—	3.00	3.00	3.00
11	Field's American Purple Top	2.6	3.00	3.00	3.00
12	N.Z. Grandmaster	—	2.98	3.00	2.99
13	Lawson's Best of All	2.6	3.00	3.00	3.00
14	Sharpe's A.1.	2.5	2.97	2.70	2.88
15	" Ne Plus Ultra	2.5	2.98	3.00	2.98
16	" Paragon	2.5	3.00	3.00	3.00
17	" Superlative	2.9	2.98	3.05	3.00
18	" Paragon	2.9	3.00	3.05	3.02
19	N.Z. Superlative	—	3.00	3.00	3.00
20	Vilmorin's Perfect	2.3	2.83	2.90	2.85
21	" Champion Purple Top	2.5	2.87	2.95	2.90
22	Webb's New Buffalo	2.4	2.83	3.00	2.92
23	" Giant King	2.7	2.75	3.00	2.83
24	Weibull's Queen	2.5	2.88	2.95	2.90
25	" "	2.5	2.95	2.95	2.95
26	" Bangholm	2.5	2.95	3.00	2.97
27	" "	2.5	2.87	3.00	2.92
28	" Ostgota II	2.6	2.83	2.80	2.82
29	Balmoral Purple Top	2.3	2.47	2.65	2.53
30	" " "	2.4	2.28	2.35	2.30
31	N.Z. Calder	—	2.00	0.30	1.67
32	Gota	2.3	2.52	2.85	2.63
33	Granhovsdet Hunsballe	1.8	2.70	1.85	2.25
34	N.Z. Sensation	1.6	2.30	0.40	1.50
35	" Yellow Flesh	1.7	1.83	0.60	1.42
36	" Wilhelmsburger	1.5	2.40	2.30	2.36
37	Sharpe's Vilmorin	1.8	2.40	1.75	2.18
38	" Hernig	2.2	2.85	2.90	2.87
39	Vilmorin's White Flesh Purple Top	2.4	2.73	2.90	2.78
40	" Yellow " Green "	1.8	2.33	2.15	2.27
41	" White " " "	2.3	2.73	2.75	2.73
42	Weibull's Balder	1.2	1.60	0.15	1.11
43	" Balder II	2.1	1.43	1.95	2.27
44	" Wilhelmsburger	1.5	0.75	0.75	0.75
45	Wilhelmsburger Otofte	1.2	1.88	1.30	1.67

Glasshouse scores were lower than field scores for all but three varieties. There was fair agreement between variety scores in the field and glasshouse ($r = .90^{**}$)

TABLE 5. ANALYSIS OF VARIANCE OF VARIETAL REACTION TO DRY-ROT

Source of Variation	All Varieties			Susceptible Varieties			Variable Varieties		
	D.F.	M.Sq.	F.	D.F.	M.Sq.	F.	D.F.	M.Sq.	F.
Total	262 ¹			160			101		
Replications	5	0.72	6.26**	5	.012	1.20	5	1.97	9.38**
Between Replications at Lincoln	3	.63	5.48**	3	.01		3	1.59	7.57**
" " Palmerston	1	.13	1.13	1	.01		1	0.06	
Between Lincoln and Palmerston	1	1.57	13.65**	1	.01		1	4.92	23.43**
Varieties	43 ¹	2.04	17.74**	26	.02	2.0**	16	2.41	11.48**
Error	214 ¹	.12		129	.01		80	0.21	
L.S.D. 5% between variety means		0.38			.12			0.53	

¹ One missing plot, one variety omitted from analysis.

** Significant at 1% level.

In the field trials, a large number of varieties, the first 28 in Table 4, had a uniform score in all replications (range between replication means less than 0.5). All these varieties had a mean score of 2.8 or more, and have been grouped as fully susceptible. Individual bulb scores of 11 of these varieties were invariably "3". Only five bulbs in the group of 28 varieties had a score of "O", and, in all, 2,905 bulbs were tested. An analysis of variance of the 28 susceptible varieties (Table 5) shows that the means of some of these varieties differed significantly, though only one was significantly different from the mean of the group. Differences between replications were not significant.

An analysis of variance of the more variable varieties (Nos. 29 to 45) is also presented in Table 5. This shows that there were significant differences between these varieties, and also that there were significant differences between replications at Lincoln, and between Lincoln and Palmerston North. Most of the between-replication variance at Lincoln resulted from the large number of bulbs scored "O" in one replication, which contained 48 of the 98 bulbs with a score of "O". This variation cannot be satisfactorily explained. At Palmerston North the proportion of plants with a score of "O" was much higher than at Lincoln, e.g., 298 out of 829 compared with 98 out of 1,302. Some varieties, viz. 31, 34, 35 and 42, had a much lower disease rating at Palmerston North than at Lincoln. As these varieties are known to be susceptible in the field, and in view of the other evidence, it appears that the test at Lincoln was more discriminating than that at Palmerston North. In consider-

TABLE 6. PROPORTION OF RESISTANT BULBS IN SWEDE VARIETIES AT LINCOLN

Variety No.	Resistant	Susceptible	Resistant/ Total %	X ² *
12	1	74	1.3	
23	1	9	10.0	
24	2	68	2.9	
26	1	84	1.2	
29	4	63	6.0	
30	4	66	5.7	
32	1	75	1.3	
33	5	78	6.0	
34	3	71	4.1	
35	5	90	3.2	
36	3	65	7.1	4.16
37	1	62	1.6	
39	4	95	4.0	
40	5	61	7.6	4.73
41	5	82	8.7	5.08
42	12	60	16.7	537.79
43	4	80	4.8	
44	29	28	50.8	53.61
45	13	79	14.1	46.39
TOTAL	103	1290		132.3
Other Varieties	0	2665	0	
All Varieties	103	3955	2.54	

* Difference from total of all varieties. Only significant X²'s shown.

ing the ratings of varieties, it would therefore seem preferable to use only the Lincoln data.

Though some varieties were completely susceptible, none was completely resistant. Some varieties, however, contained bulbs with a score of "0" in such proportions that their failure to produce lesions cannot be attributed to chance failure of the test procedure (See Table 6.). These plants have been classified as "resistant," and the proportion in each variety is shown in Table 6.

One variety (44) was outstanding, and with two others (42, 45) accounted for half the resistant bulbs.

In addition, all the varieties in the variable group contained a proportion (7-97%) of bulbs with scores of "1" and "2". These bulbs were probably more resistant than those with a score of "3", but it is doubtful whether they were sufficiently resistant to withstand attack in the field.

DISCUSSION

Significant differences were found between variety means, and resistant plants were not randomly distributed among all the varieties. Thus, there is little doubt that both variety means, and variation within varieties, are inherent varietal characteristics. Some varieties were represented by more than one line in the trials. Lines of any one variety occurred together in the susceptible or variable groups. It is plain that no variety can be graded "resistant", though some varieties did contain what appeared to be resistant plants. A progeny test should show whether this resistance is genetically determined.

CONCLUSION

From the results of the crop surveys reported in this paper, it may be concluded that the variety Wilhelmsburger is less likely to be severely damaged by dry-rot than other varieties grown in New Zealand.

Several of the varieties tested in inoculation trials contained a number of resistant plants. Of these, Weibull's Balder, Weibull's Wilhelmsburger and one line of Wilhelmsburger Otofte of unknown origin were outstanding.

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SEED DISINFECTION

X. EFFECT OF SEED PROTECTANTS ON EMERGENCE OF SPINACH

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Summary

Of 40 fungicides tested 13 gave effective protection of spinach seed against pre-emergence damping off in soil artificially inoculated with *Pythium ultimum*, Trow. Effective substances were based on the following chemicals: cuprous oxide, dichlone, phenyl mercuric dinaphthyl methanedisulphonate, methoxy ethyl mercury, ethyl mercury phosphate, thiram, ferbam, copper 8 quinolinolate, nitrosopyrazole and captan.

INTRODUCTION

Pre-emergence damping off of spinach seed (*Spinacea oleracea* L.) is generally caused by the presence of soil fungi. A large number of chemicals have been recommended for general seed treatment, but as some of these materials are more effective than others it is necessary to specify the types of seeds they can protect. Tests here described were carried out to select the most effective materials for protecting spinach seed from pre-emergence losses.

MATERIALS AND METHODS

Altogether 40 chemical preparations of different composition were tested. These may be conveniently grouped as follows:

1. Copper compounds: Cupric carbonate (56% copper, 0.035% chloride, 0.2% sulphur, 0.25% ferrous oxide); Red Cuprocide (94% cuprous oxide); Yellow Cuprocide (90% cuprous oxide).

2. Quinones: Spergon (98% chloranil, i.e. tetrachloro-p-benzoquinone); Phygon (98% dichlone i.e. 2, 3, dichloro, 1-4 naphthoquinone); Phygon XL (50% dichlone).

3. Organo-mercury compounds: Agrosan GN (1% tolyl mercury acetate); Ceresan (2% ethyl mercury chloride); Agrimax M (4% phenyl mercuric dinaphthyl methanedisulphonate); Agrimax A (4% phenyl mercuric dinaphthyl methanedisulphonate, combined with a growth promoting substance and an insecticide); Verisan (1.5% methoxy ethyl mercury); Venturicide (2.5% phenyl mercury chloride); Agrandin I (3.7% alkoxy alkyl mercury); Barbak (8% mercuric phenyl cyanamide); Calomel (85% mercurous chloride); Ceresan NI (5% ethyl mercury phosphate); Ceresan M (7.7% ethyl mercury p-toluene sulphonate); Leytosan (1% mercury); Semesan (1% ethyl mercury phosphate).

4. Dithiocarbamates: thiram (98% tetramethyl thiuram disulphide); Nomersan (10% thiram); Fernasan (50% thiram); Thiroadust (75% thiram); ferbam (98% ferric dimethyl dithiocarbamate); Fernspray (70% ferbam); cupram (98% cupric dimethyl dithiocarbamate); CPD (98% cupric pentamethylene dithiocarbamate); ziram (98% zinc dimethyl dithiocarbamate); Aaphythora (70% zineb, i.e. zinc ethylene bisdithiocarbamate).

5. Miscellaneous compounds: 8 quinolinol sulphate: 8 quinolinol; 8 quinolinol benzoate; zinc 8 quinolinolate; copper 8 quinolinolate; Dow 9 B (50% zinc trichloro phenate); Anticarie SD (20% hexachlorobenzene); Chloroble (10% hexachlorobenzene, 20% sulphur); 36L (98% 1-(p-sulphamylephenyl)-3:5-dimethyl-4-nitrosopyrazole); Folosan (16% pentachloronitrobenzene); Flit 406 (50% captan, i.e. n-trichloromethylthio-tetrahydrophthalimide).

Materials were applied as percentages of seed weight and even distribution was ensured by agitating both materials and seed in a mechanical shaker for five minutes. A potting mixture of steam disinfected volcanic soil was inoculated at the rate of 2.5% by weight with sand and oatmeal cultures of *Pythium ultimum* Trow. Before use, inoculated soil was held for 14 days to allow the fungus to penetrate through the soil. Before potting, soil moisture was adjusted to 35% of its water holding capacity. Cultural practices employed and the method of recording were described previously (Jacks, 1951). Each replicate was sown with 50 spinach seeds, there being five replicates for each treatment. All tests were repeated and results given in tables represent the means from two tests. Percentages were transformed to equivalent angular values and only these are given in the tables.

RESULTS

A preliminary selection of substances was carried out at the dosage rate of 2% of seed weight. Results are given in Table 1.

In this test the 5% and 1% levels of significance were used for evaluation of the efficacy of substances.

The following materials significantly increased emergence as compared with checks:—

Yellow Cuprocide, Phygon, Phygon XL, Agrimax M, Verisan, Ceresan NI, Leytosan, thiram, Fernasan, Thirodust, ferbam, Fernspray, ziram, 8 quinolinol sulphate, copper 8 quinolinolate, 36L and Flit 406.

Significant depression of emergence as compared with checks resulted from applications of Agrimax A, Calomel, Aaphythora, 8 quinolinol, 8 quinolinol benzoate, and zinc 8 quinolinolate. Ceresan NI and 36L brought about significant reduction of diseased seedlings as compared with checks.

In previous experiments with seed disinfectants (Jacks, 1952), it was found that dosage estimation was necessary for lettuce, pea, bean, beet, turnip, tomato and celery seeds which were found to be sensitive to certain substances. Materials effectively increasing emergence over check in preliminary tests were therefore tested at three different dosage levels, viz. at 0.5, 1.0 and 2.0% of seed weight. Results are given in Table 2.

TABLE 1. PRELIMINARY TESTS: MEAN PERCENTAGE (EQUIVALENT ANGLES) EMERGENCE OF SPINACH SEEDLINGS FROM THREE TESTS
(Seed Treated at 2% of Weight.)

No.	Treatment	Healthy	Diseased
1	Check	39.7	22.0
2	Cupric carbonate	44.4	26.7
3	Red Cuprocide	37.7	24.5
4	Yellow Cuprocide	48.5	23.3
5	Spergon	36.3	23.3
6	Phygon	46.0	29.0
7	Phygon XL	45.6	27.5
8	Agrosan GN	40.6	22.1
9	Ceresan 2	42.8	21.4
10	Agrimax M	46.4	23.9
11	Agrimax A	33.6	23.8
12	Verisan	50.7	27.4
13	Venturicide	42.8	27.0
14	Agranin I	44.1	28.1
15	Barbak	40.4	27.1
16	Calomel	30.0	24.7
17	Ceresan NI	58.0	11.1
18	Ceresan M	44.2	26.0
19	Ieytosan	49.4	26.4
20	Semesan	36.5	28.5
21	thiram	48.4	28.1
22	Nomersan	40.8	21.0
23	Fernasan	50.4	24.3
24	Thiroadust	49.0	21.1
25	ferbam	46.5	25.6
26	Fermspray	49.7	26.0
27	Cupram	35.4	18.4
28	CPD	35.9	28.8
29	Ziram	45.0	24.5
30	Aaphythora	33.8	22.9
31	8 quinolinol sulphate	46.7	22.0
32	8 quinolinol	30.5	28.1
33	8 quinolinol benzoate	31.9	19.1
34	zinc 8 quinolinolate	33.5	18.5
35	copper 8 quinolinolate	53.9	22.5
36	Dow 9 B	39.2	18.5
37	Anticaric SD	34.8	20.6
38	Chloroble	37.2	28.0
39	36 L	56.9	16.8
40	Folosan	41.3	21.7
41	Flit 406	50.8	25.6
Difference required for significance at:			
	5%	5.2	3.7
	1%	8.3	5.6

Comparisons between figures obtained were made at the 1% level of significance. Most materials effectively increased emergence at the dosage rate of 1% of seed weight, although effective substances gave significant increase in emergence at other dosage levels. Leytosan, ferbam, ziram and 8 quinolinol sulphate failed to improve emergence over check.

TABLE 2. MEAN PERCENTAGES EMERGENCE (EQUIVALENT ANGLES) OF SPINACH SEEDLINGS, FROM TWO TESTS
(Seed Treatment at 0.5, 1.0 and 2.0% of weight)

No.	Material	Treated at 0.5% of weight		Treated at 1.0% of weight		Treated at 2.0% of weight	
		Healthy	Diseased	Healthy	Diseased	Healthy	Diseased
1	Check	37.1	21.8	33.2	18.5	34.2	20.6
2	Yellow Cuprocide	45.2	25.9	48.7	24.4	51.7	18.0
3	Phygon	42.9	27.7	46.7	25.5	48.6	30.4
4	Phygon XL	38.5	24.8	56.3	30.7	42.9	25.5
5	Agrimax M	36.4	19.3	45.3	20.6	44.6	20.0
6	Verisan	49.1	30.1	46.6	22.4	42.9	19.6
7	Ceresan NI	48.7	21.9	50.6	20.8	47.8	12.4
8	Leytosan	47.6	23.7	43.4	26.9	41.0	19.9
9	thiram	43.3	20.6	45.8	26.0	48.1	21.8
10	Fernasan	43.2	25.2	56.4	26.1	50.8	17.4
11	Thiroadust	45.5	22.9	52.5	21.1	50.8	17.3
12	ferbam	42.8	24.9	43.4	23.3	39.8	13.2
13	Fermspray	40.9	20.4	48.1	25.6	45.2	22.2
14	Ziram	43.4	22.6	41.3	23.1	42.8	18.3
15	8 quinolinol sulphate	38.9	21.5	43.1	22.3	37.6	15.6
16	copper 8 quinolinolate	50.0	25.6	53.8	23.0	42.9	14.6
17	36 L	48.7	21.8	50.9	14.5	52.7	14.3
18	Flit 406	48.6	23.6	49.7	26.5	47.2	19.7
Difference required for significance:							
	5%	9.1	3.8	9.1	3.8	9.1	3.8
	1%	11.9	6.1	11.9	6.1	11.9	6.1

TABLE 3. MEAN PERCENTAGES EMERGENCE (EQUIVALENT ANGLES) SEEDLINGS FROM TWO TESTS
(Seed Treated at 1% of weight)

No.	Treatment	Healthy	Diseased
1	Check	30.0	14.5
2	Yellow Cuprocide	49.0	19.3
3	Phygon	46.6	26.6
4	Phygon XL	55.2	29.5
5	Agrimax M	48.3	26.8
6	Verisan	48.3	24.5
7	Ceresan NI	55.8	21.3
8	thiram	52.0	25.7
9	Fernasan	55.0	30.7
10	Thiroadust	60.7	23.5
11	Fermspray	54.1	27.4
12	copper 8 quinolinolate	53.1	27.7
13	36 L	53.6	20.1
14	Flit 406	50.4	28.0

Difference required for significance

at: 5%
1%

11.0
14.7

4.0
6.0

Final tests were carried out with seeds treated at 1% by weight. The 1% level of significance was used for comparison of the effectiveness of treatments. Results are given in Table 3.

All substances significantly increased emergence over check. Differences between substances were not significant.

DISCUSSION

Considerable variations were observed in the effectiveness of substances within chemical groups. Thus of the copper compounds, Yellow Cuproside only was effective, whilst of the quinones, dichlone was more effective than chloranil. Mercury combined with methoxy ethyl, ethyl phosphate and dinaphthyl methanedisulphonate was more effective than other formulations. The addition of a growth-promoting substance and an insecticide to mercuric dinaphthyl methanedisulphonate reduced the efficacy of this compound. Of the dithiocarbamates, a compound containing less than 50% thiram was not effective, formulation improved the efficacy of ferbam, whilst cupram, CPD, ziram and zineb were not effective in protecting spinach seed from pre-emergence damping off. Copper 8 quinolinolate, nitrosopyrazole and captan were the most effective of other compounds tested.

An increase in emergence of both healthy and diseased seedlings was brought about by seed dusting. Counts of diseased seedlings included plants showing obvious symptoms of *Pythium* injury as well as plants showing only very slight lesions. As the latter may have survived and grown into plants similar to those derived from healthy seedlings it is probable that total emergence (final stand) from treated seed could have reached greater proportions than those given in the tables. Differentiation, at the time of recording, between healthy and diseased plants, independent of the degree of injury, gives a more critical appreciation of the degree of effectiveness of substances used in seed protection. Results suggest that treatments appear to bring about increased vigour of plants enabling a greater number of seedlings to survive pre-emergence and to resist post-emergence damping off.

ACKNOWLEDGEMENT

Appreciation is expressed to Mr. W. B. Taylor of the Applied Mathematics Laboratory, Department of Scientific and Industrial Research, for statistical analysis of results.

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STUDIES IN USE OF AGRICULTURAL LIMESTONE

I. CHEMICAL AND PHYSICAL PROPERTIES OF SOUTH ISLAND (N.Z.) AGRICULTURAL LIMESTONES

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Summary

1. Results are presented of a survey of the chemical and physical properties of the agricultural limestones commercially available in the South Island of New Zealand during the years 1946-47; the ultimate purpose being to discover if any one property or group of properties exerts a decisive influence on rate of solution in the soil. The investigation of the latter point is reported in the succeeding paper of this series.
2. The limes¹ examined, representing eighty per cent or more of the lime used, are invariably low in content of magnesium and phosphorus, and contain no major nutrient of significance not reflected in their neutralising power as usually determined. Micro-nutrients were not determined.
3. In structure the limestones fall naturally into two groups, described here as the compact and the shelly limes, between which there is a marked and significant difference in physical properties and behaviour on crushing.
4. An analysis is presented of the fineness of grinding curves of samples collected over a period of six years. The most significant differences occur in the percentage of material coarser than B.S.S. 18 mesh, and grounds are given for the adoption of a proposed single-value standard of fineness based on that mesh. Wet sieving, by the slaking of aggregates, gives results significantly different from dry sieving, and in some cases very different, particularly in the case of the shelly limes. Compact limes yield a significantly higher proportion of superfine material on crushing. In consequence of this and of their greater aggregation, shelly limes appear coarser than compact limes that are equally well ground in respect to their coarser fractions.
5. The physical properties of the limestones vary in extreme degree. Characteristic differences are reported in respect of equilibrium moisture content, porosity, grindability (hardness), reactivity index and the form of the crushed particles. The equivalent calcite surface (external) of standard-sieve separates of the limes is expressed in terms of an extremely rapid surface reaction with N/10 oxalic acid. This initial reaction is followed by a much slower prolonged secondary reaction, which is more an expression of internal surfaces. The shelly limes, as a group, differ significantly from the compact limes in respect of most of the physical properties measured. Shelly limes are more porous, more easily ground and display on the average 50% greater equivalent calcite surface than is the case with the compact limes.
6. The equivalent calcite surface of the limes varies by 450%, fineness being constant, and is shown to be a function of purity, porosity and particle shape. The simple measure of apparent volume, loose packed, of equivalent weights of the standard sieve separates, integrates the influence of these three properties, and displays a correlation coefficient of 0.935 with the determined values for equivalent calcite surface, and also (as demonstrated in the succeeding paper) a similar correlation coefficient of 0.944 with the measured rates of solution in the soil. Differences in chemical reactivity appear to be due to differences in degree rather than in kind of carbonate surface exposed.

¹ Whenever in this paper the commonly used term "lime" is employed for brevity and convenience it refers to agricultural limestone and not to burnt lime or calcium oxide.

INTRODUCTION

New Zealand farmers now use considerably more than a million tons of crushed agricultural limestone every year, and the rapid growth

of this practice during the past twenty-five years has played a major part in the expansion and intensification of primary production in this country. During that time the community has probably spent, directly and indirectly, no less than £35 million on the production and transport of lime and its application to our farmlands. Yet compared with the obvious importance of the lime industry, the amount of scientific work that has been done in New Zealand relating to the production and use of lime is small. In contrast with technical developments in other branches of farm practice, the use of lime is still governed more by empirical methods and custom than by scientific knowledge and precision.

Many practical questions asked by farmers cannot be met with precise and confident answers. Among such questions are the following: the most profitable amount of lime to apply at one time in various circumstances; the optimum degree of fineness, and the influence on this of the type of limestone used; the rates of loss by leaching on different soil types and in the different climatic zones of this country; the depth below the surface at which the calcium of past dressings is still usefully available to plants; whether quick solution, as of fine carbonate, is as conducive to rapid loss by leaching as has commonly been supposed; how far one may go in building up a reserve of lime in the soil without incurring too great an annual loss by leaching; and lastly the influence of soil type on all these questions—these are practical questions to which as yet we have only partial answers, and in some cases mere guesses.

Even the concept of lime requirement itself is lacking in any real definition, not only in respect of the purpose which the lime is intended to fulfil and the quantity required in relation to soil conditions, but also as affected by the soil's status in other nutrients and the coarseness, solubility and longevity of the dressing applied. By way of illustrating the last two points, recent publications of Aslander (1952), and Crowther and Walker (1952) may be quoted. Aslander demonstrated that the lime need of strongly acid soils can be reduced to nil if a sufficient quantity of the other major nutrients is supplied, while Crowther and Walker have shown in Great Britain that a succession of crops responded as well to dressings at standard lime-requirement rates of coarse "limestone dust" as to equal dressings of finely pulverised limestone all passing 100 B.S.S. The limestone dust consisted of the $\frac{1}{4}$ inch screenings from a road-stone crushing plant, with only 22% 100 B.S.S., (Walker, pers. com.), and the amount dissolved during the first few years of the trial must have been very considerably below the lime requirement of the soil as estimated by conventional laboratory methods. As further evidence of the present vagueness of the concept of lime requirement, one need only mention the recent striking discoveries on the influence of molybdenum on the lime needs and responses of pasture and crops grown on certain soils.

The present series of studies, of which this paper is the first part, is an attempt to provide more precise answers to some of these questions. In pursuance of the recommendations of the Agricultural Lime Investigation Committee (1940), referred to again below, an investigation was begun in 1947 on the problem of the fineness of grinding of agricultural lime in its relation to the physical and other properties of the limestones employed. This paper reports the results of a preliminary survey of

the chemical and physical properties of the South Island agricultural limestones commercially available in 1947. An account of the investigation of the influence of these properties on the solubility of limestones in the soil, together with a discussion of the extensive literature on that subject, is reserved for the succeeding paper in this series.

PREVIOUS OBSERVATIONS

Interest in the use of lime in this country first assumed significant proportions during World War I, stimulated no doubt by the shortage of imported fertilisers. During the war years and extending well into the 'twenties there appeared a long sequence of articles and reports in the N.Z. Journal of Agriculture, chiefly from the pens of B. C. Aston and Andrew McTaggart, publicising the benefits of liming, and reporting on New Zealand's resources of limestone and means of exploiting them for agricultural purposes. It was by this time becoming more generally recognised that limestone did not require burning for its effective use on the land, so that attention could be turned to many deposits previously considered too low in quality to merit the cost of burning. Aston's published analyses demonstrated the widespread occurrence throughout both Islands of limestones of sufficient quality to warrant their commercial exploitation for agricultural use, while Morgan's comprehensive report (1919) gave detailed descriptions of all known outcrops, supported by a large amount of analytical data. Wild and Speight (1919), in a survey of Canterbury limestones as a possible source of phosphate, reported the generally low level of the phosphate content, together with the widespread occurrence of phosphatic concretions in quantities too small and inaccessible to be of economic value. Incidentally, they seem to have been the first to point to the advantages of cheaply produced coarse carbonate and of easily worked low grade limes. These reports established the fact that New Zealand's limestones, with few exceptions, belonged to the more soluble high-calcic type, being only slightly enriched with magnesium and phosphate. Few of them were found to contain more than 3%, the majority less than 1% of magnesium carbonate, while their content of phosphate was even lower, rarely amounting to as much as one per cent, and in most cases very much less. Very few truly phosphatic or dolomitic limestones were encountered. Little, however, was recorded at that time regarding the physical properties of the limestones.

During the 'thirties the quality of our lime resources came under more critical review. Grimmett and Denz (1933) noted the considerable variation in the ease or difficulty with which the limestones could be pulverised, and observed correctly that the purer limestones are frequently the harder to crush. They reported a very wide variation in the fineness of grinding of the commercial supplies then available, and noted the occurrence of some excessively coarse samples; and while suggesting that coarseness might enable farmers to stock their land cheaply with reserve calcium, they stressed the need for some established standard of fineness and for a means of assessing the availability of the calcium in different types of limestone. Hudson *et al.* (1937) reported significant differences in the chemical reactivity of limestones. Comparing the effectiveness of different limes in bringing about the reversion of superphosphate, they found the fine grained limes derived from foraminifera considerably more effective than those derived from mollusc shell, and that this structural difference had more influence on the reaction than

the differences in fineness of grinding of the limes under test. Fife (1938) reported on the poor quality of a large proportion of the New Zealand commercial supplies of burnt lime, and found them in most cases a considerably more costly form of calcium than crushed carbonate. The presence of cobalt in many South Island limestones in quantities sufficient to benefit the health of lambs reared on the limed pastures was demonstrated by Dixon and Kidson (1940, 1941) and fuller reports on the cobalt content of South Island and North Island limestones were published by Stanton (1944) and Maunsell (1945).

The Agricultural Lime Investigation Committee (1940), appointed in 1939 to investigate the organisation and efficiency of the lime industry, reported *inter alia* on the great variations in the quality of agricultural lime sold throughout the Dominion in respect of purity, hardness, moisture content and fineness of grinding, and noted the marked physical dissimilarity between hard and soft stones. They recorded the commonly held beliefs that easily crushed stones need less reduction in particle size than do the hard stones, and that a coarse product does not leach so readily as a fine one. There was some divergence of opinion as to the most desirable degree of fineness, but general agreement in the industry that a more coarsely ground lime is easier to handle and spread and can be produced very much more cheaply. The Committee included in its recommendation that further research should be carried out with a view to accurate assessment of the relative merits of hard and soft limes, and finely and coarsely ground limes.

In quick response to this suggestion, Jones (1941) measured the "reactivities" of a number of New Zealand agricultural limestones in terms of the rate of solution of a standard coarse sieve separate in 1% acetic acid. The limestones were shown to have characteristically different rates of solution, with a range of 300% between the slowest and most rapid solution. In general, the dense hard stones were the least reactive, and it was suggested that the test might serve as an indication of those limestones requiring extra fineness of grinding. Davies (1949) (1951) improved the technique of measurement and reported briefly on the reactivities of a large number of limes on sale to farmers throughout New Zealand. He found a broad correlation with the hardness of the stone. The North Island limes fell entirely within the medium—low range of reactivity, while the South Island limes proved much more diverse, including all the least reactive as well as an extensive range of more highly reactive limestones. Davies also reported (1951) on the fineness of grinding of the limes examined. His observations are referred to later in this paper.

Some measure of the properties and the degree of variability of New Zealand agricultural limestones had thus been built up, and one very thorough trial at Marton (Doak, 1941; Elliott and Lynch, 1941) had compared the behaviour of a hard shelly lime and a moderately hard chalky lime, both coarsely and finely ground, when used as pasture topdressing. It was, however, considered desirable to make a more comprehensive survey of the agricultural limes commercially available in the South Island, both as to the native rock and the crushed product, with a view to determining the full range of variability in the existing supplies, and whether there might be any one property or group of properties of the limes capable of exerting a decisive influence on their rates of solution in the soil.

PROPERTIES OF SOUTH ISLAND AGRICULTURAL LIMESTONES

The purpose of this survey was solely to obtain a measure of the range and variety of characteristics to be found in the main commercial supplies, with the object of ensuring that all significant variations were included in the collection of limes which was to be submitted in due course to solubility tests. It was not the intention to obtain any definitive data on the output of individual limeworks, for which purpose a more extensive series of samples would have been necessary. The generally high significance of the differences recorded is justification of the number of samples employed. At various dates during 1946 and 1947 reliable samples of the crushed limestone, as sold, were taken at 31 limeworks, either by the writer or other College officer, or by an officer of the Extension Division of the Department of Agriculture. All the major limeworks in the South Island were included. Samples were also included from a North Canterbury deposit of soft chalk, not hitherto worked commercially, since it provided an extreme example of the porous fine grained type of lime. There were in addition about an equal number of smaller suppliers not included in this survey, many operating only periodically with portable crushers, but the limes included probably accounted for more than 80 per cent of the lime used. More than twice as many additional samples from the 31 works were received from time to time, in some cases through less independent or reliable sources, and these served to confirm the generally representative nature of the samples reported on here. In addition to the crushed samples, at least four typical hand specimens of the rock were obtained from each quarry. In the case of the Canterbury, Otago and Southland works, almost all of these were selected at the quarry face by the writer.

CHEMICAL PROPERTIES

The ground limestones were examined for total carbonates or "titratable bases", determined by their power to neutralise $N/2$ hydrochloric acid, and expressed as $CaCO_3$ equivalent; also, for acid soluble CaO , MgO and P_2O_5 , (soluble in hot $2N$ hydrochloric acid) determined by the usual methods. The results are presented in Table 7, Columns 1-4. The distribution of carbonate contents is shown in Table 1. It is not safe to generalise too freely about the averages for different provinces. Low averages are largely due to the inclusion of one or two really poor samples. As shown later, (see Table 5) the shell limestones tend to be of lower purity and have a significantly higher magnesium content than the more homogeneous or compact limestones. The purity of the output from every quarry inevitably varies to some degree, in some cases much more than in others. One quarry from which thirteen samples were received over a period of twelve years showed an extreme range of 14.5% in carbonate contents. Such wide variation however is unusual. Over a period of six years the testing of 89 samples from 24 limeworks, from which two or more samples were received in each case, revealed an average variation $\pm 2.7\%$ in the purity of the product.

Regarding constituents other than calcium carbonate, the general evidence of the earlier analyses is confirmed. South Island agricultural limes, with the exception of one or two minor instances not included in this survey, belong entirely to the high-calcic type. The magnesium content is uniformly low, ranging from 0.15 to 1.47% MgO , with a

TABLE 1. DISTRIBUTION OF CARBONATE CONTENTS OF AGRICULTURAL LIMES FROM 31 SOUTH ISLAND LIMEWORCS:

(a) BY PROVINCES; (b) BY PURITY RANGE

(a) Province	Limeworks	Mean percentage of carbonate
Nelson	5	91.3
Marlborough	4	82.9
N. Canterbury	7	80.7
Mid. & S. Canterbury	4	78.7
Otago	4	91.1
Southland	7	74.3
	31	Mean 82.2%

(b) Purity range	Samples
90-100% carbonate	10
80-90 % "	6
70-80 % "	10
60-70 % "	3
< 60 % "	1

mean value of 0.53%. Only two values exceed 1%, these being for two rather low grade Southland samples. The phosphate content is likewise uniformly low, ranging from 0.06 to 1.08% of P_2O_5 , with a mean value of 0.25%. Only in one case, a North Canterbury limestone, is there more than 1% of P_2O_5 . The total contents of $CaCO_3 + MgCO_3$ expressed as $CaCO_3$ -equivalent, calculated on the assumption that acid-soluble CaO and MgO are present wholly as carbonates, agrees closely with the figures for titratable bases, the mean difference between the two values being less than one per cent; and it is evident that these limestones contain no major ingredient of any significance that is not reflected in their neutralising power as usually determined. Their content of micro-nutrients was not determined.

Davies (1951) noted differences in the carbonate content of the different sieve fractions of some of the lower grade limes. In the present survey seven limestones, representative of the most distinctive types, were each separated into four water-washed sieve fractions, 10-20, 20-40, 40-80 and 80-150 mesh respectively. The carbonate contents of these suggest that the fine grained homogeneous limestones display little or no segregation of carbonate when pulverised, except for a tendency to enrich the finer fractions, due apparently to the greater shattering of brittle veins of secondary calcite of exceptionally high purity. The heterogeneous shelly limes of medium to low purity, on the other hand, show a considerable enrichment of carbonate in the 20-80 mesh range due to a concentration of shell splinters, and a marked drop in the

purity of the 80-150 mesh fraction due to the accumulation of sandy impurities, chiefly quartz and glauconite. In one extreme case the carbonate content of the separates was found to vary from 90% down to 69%. This segregation of carbonate receives further consideration on page 164.

PHYSICAL PROPERTIES

The Physical Structure of the Limestones

A brief description of the physical characteristics of each of the limestones is given in Table 7, and although no useful purpose might be served by recording more details of their individual macroscopic features, a review of their main characteristics and differences seems desirable. Three ancient rocks, probably of palaeozoic age, stand out from the rest; two of them are finely crystalline limestones and the third a white marble. The term "crystalline" is used in the sense that the crystalline structure is noticeable to the unaided eye. All three are unusually hard and dense and apparently devoid of organic structure. The remainder of the limestones examined belong to the Tertiary era, and to the Oligocene period in most cases.² However, conditions of deposition and subsequent geological history have varied to produce limestones of great diversity. They fall naturally into two groups: those deposited in deep water and derived largely from the fine-grained calcareous remains of species of foraminifera, too minute to be apparent to the eye; and those that accumulated in comparatively shallow water and derived mainly from the broken calcareous structures of Polyzoa and the shells of Branchiopods and Molluscs.

To the former group belong the relatively homogeneous white and pale coloured limes of the Amuri Series, which occur extensively throughout North Canterbury and Marlborough. Some of these are only moderately hard, have a platy fracture and retain a fine-grained porosity of a high order; others have become so dense as to be flinty in texture, conchoidal in fracture, low in porosity and seamed with fine veins of secondary calcite. The latter types are of course much the harder. In the case of these more or less homogeneous fine grained limestones, as also of the three ancient crystalline stones, there is little difference, when pulverised, in the form of the coarse and the finer particles, except that the latter are sometimes a little more sharp and splintery (see Fig. 1, Plates A and B.). This rule certainly applies down to the fineness of 150 mesh, and probably much further, and is due to the fineness of their texture. The general form of the particles is that of sharply angular irregular polyhedra. Limestones of this type are referred to hereafter as the compact limestones. This term, as used, serves conveniently to distinguish them from the coarsely porous shelly limes, and does not preclude the presence of a fine grained porosity, in some cases of a high order.

The second group, comprising 16 out of the 32 limestones, may be termed the heterogeneous or shelly limestones, and these predominate from Mid-Canterbury southwards. These, likewise, have experienced varying degrees of induration by recrystallisation of calcite, and range from dense noticeably crystalline stones containing embedded shell fragments visible on close inspection but otherwise indistinguishable from

² The writer is indebted to Dr. B. H. Mason, lately of Canterbury University College, for a geological description of these limestones.

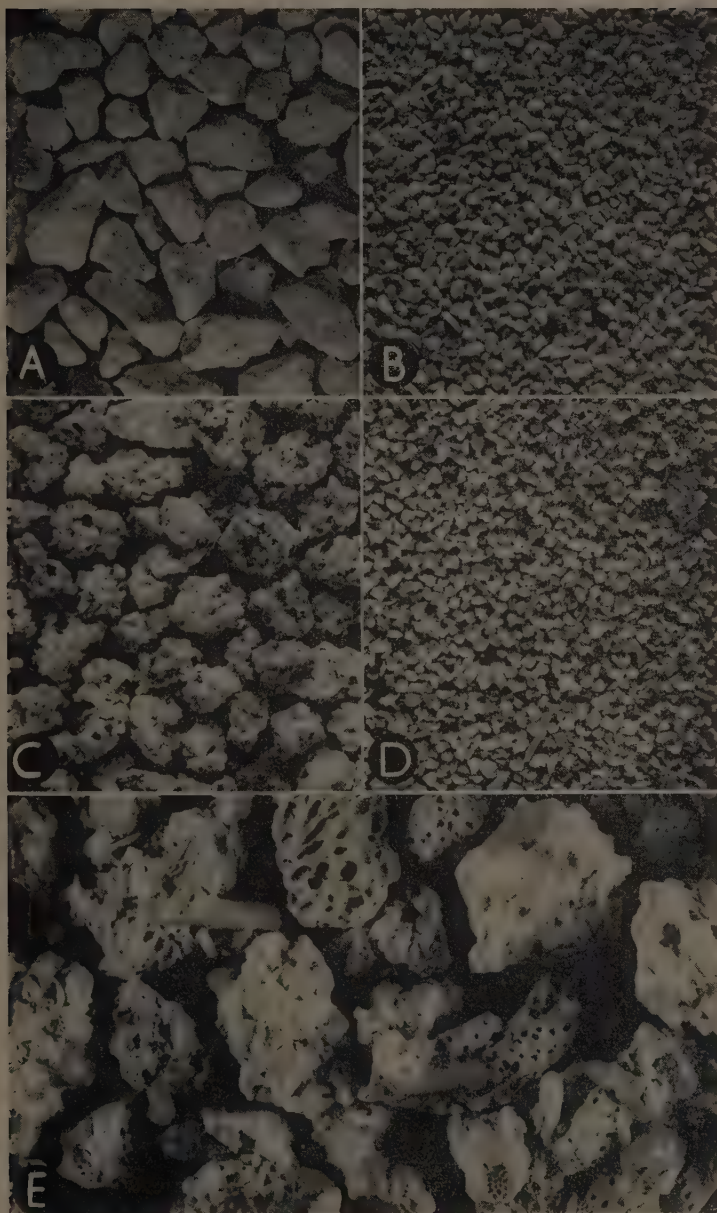


Fig. 1: A and B—The 20-40 and 80-150 mesh separates of compact Limestone N.

C and D—The corresponding separates of shelly limestone T. Note the greater similarity of the finer separates.

E—The 10-20 mesh separate of Limestone U illustrating the irregularity and coarse grained porosity of shelly limestone particles.

×12 Photos: R. C. Blackmore,

the compact limestones, to loosely cemented aggregates of shell sand, with quartz, glauconite and haematite as major impurities. The majority belong to the less altered, more porous variety. The coarser fragments of these limestones appear to retain the cavities and the organic structural irregularities so apparent in the massive stone, giving them a high specific surface. This is well shown in Fig. 1, Plate E. In the finer fractions, however, these limestones are seen to have fallen apart into denser irregular shell fragments. (Fig. 1 Plates C and D.) The pulverising process appears to eliminate a proportion of the coarse grained porosity, and the finer particles, though still somewhat irregular in form, are more similar to corresponding particles of the compact limestones in density and presumably in hardness, than might commonly be supposed. It would seem that there is less difference in what might be called the effective hardness of the limes when pulverised than would be inferred from the differences in their ease of crushing or their rapidity of weathering at exposed outcrops.

In consequence of the above structural differences limestones of the various outcrops possess quite distinctive features. The colour and texture of the surfaces, the organic structures and the types of porosity they involve, the type of fracture and shape of particle produced, and the presence and size of noticeable constituents such as grains of glauconite, all are so distinctive that a close examination of washed fragments will usually enable their source to be identified if a previous sample from the same quarry is on hand. The attempt was made to evaluate these structural differences and their effects on the crushed products, by means of the series of physical measurements recorded below. A general discussion of the inter-relationships between these physical properties will be found in the concluding section of this paper.

Fineness of Grinding

It would be more accurate to use the term "fineness of crushing" here, since these products are the result of a crushing or pulverising rather than a grinding process. (Gross, 1938). The term "fineness of grinding", however, is retained since it is the one so commonly in use. In contrast to the consistency of the physical structure of the different limes, fineness of grinding is an independent and more variable character, and it was accordingly assessed by reference to a wider range of samples. As it is virtually impossible to reach an end point in sieve separations, the sub-sampling and sieving techniques were carefully standardised. Results from the dry sieving of 70 samples, representing 33 limeworks, received during the period 1946-52, are summarised in Fig. 2. They conform to the principle that applies generally to pulverised materials (Robinson, 1936; Salter and Schollenberger, 1940), that smooth curves are obtained when summation percentages are plotted against the logarithm of particle size, or, as in the present case, of mean sieve aperture. The size-distribution curves for 80% of the samples tested lie between the dotted lines, leaving 10% coarser and finer than these limits. The lower curves correspond to the finer grinding. The sieves used were not standard sieves, but their mean apertures were determined, and the method of presentation enables any known scale of sieve apertures to be applied to the curves. For example, comparison can be made between these curves and the standard of fineness adopted in 1951 by the Lime Advisory Committee of the N.Z. Department of Agriculture (1951). By

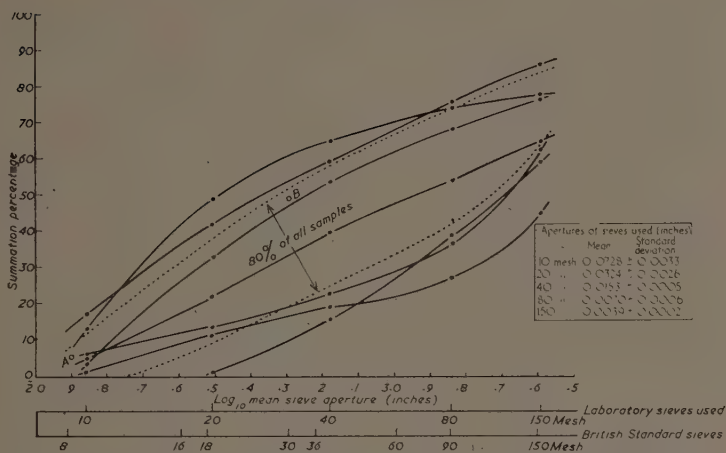


Fig. 2—Typical size-distribution curves for South Island agricultural limes. The curves for 80% of the 70 samples examined lie between the dotted lines.

applying the British Standard Sieves scale to Fig. 2 the two stipulated limits have been plotted. (Points A and B). It was found that approximately 20% of the samples exceeded the limit of five per cent retained on B.S.S.8 mesh, (mean aperture 2.06 mm.) and 12% exceeded the limit of 50% retained on B.S.S. 30 mesh (mean aperture 0.50 mm.).

The slope and form of the curves are not without interest. The convergence to a narrow range at the coarse end is doubtless due to the similarity in the screens employed in the crushing plants. The greatest and most significant differences occur in the percentages of material coarser than 20 mesh, or thereabouts, this being reflected in the divergence of slopes in this portion of the curves. Thereafter, the curves become more nearly parallel, with the result that the percentages of material passing 80 mesh are to a large extent complementary to the amounts of > 20 mesh material, there being a negative correlation coefficient of -0.652 (significant at 1% level) between these two quantities. It would therefore seem possible, with little error, to define the fineness of grinding of any one of these limestones in terms of a single value, namely, the percentage retained on B.S.S. 18 mesh, which is almost identical with the 20 mesh used for these tests.

The following single-value scale of fineness is suggested:

Very coarse	45%+ retained on B.S.S. 18 mesh				
Coarse	30-44%	"	"	"	"
Medium	15-29%	"	"	"	"
Fine	5-14%	"	"	"	"
Superfine	Under 5%	"	"	"	"

These limits are shown in Fig. 3 against the general distribution of fineness curves. The medium class lies centrally in the zone of greatest frequency. The adoption of B.S.S. 18 mesh for this purpose would

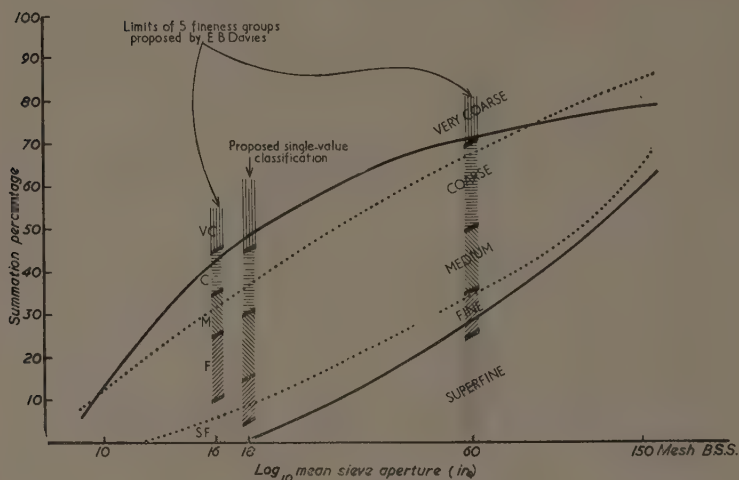


Fig. 3—Comparison of two proposals, a single-value and a two-point classification of fineness. Compare with Fig. 2.

appear to allow better discrimination than the use of 16 mesh or coarser, owing to the rapid convergence of *this* end of the curves. The justification for such a scale is considered more critically below.

The fineness of limes produced in the various provinces when classified in the above manner is shown in Table 2, together with the mean percentages of material coarser than B.S.S. 18 mesh, giving equal weight to all limeworks. In terms of the latter criterion, North Canterbury and Southland limes are each significantly coarser than the rest (at 2% and 5% levels respectively.). There is a tendency for the hard limes to be more finely ground than the medium to soft stones, but there are several exceptions. Actually none of the hard stones are coarsely ground, but some of the soft stones are finely ground.

TABLE 2. FINENESS OF GRINDING OF LIMES PRODUCED IN SOUTH ISLAND PROVINCES

Province	Samples Tested	Very Coarse	Coarse	Medium	Fine	Superfine	Mean Per cent > B.S.S. 18
Nelson	7	— ^e	—	4	1	2	18
Marlborough	5	—	—	3	2	—	17
N. Canterbury	21	3	8	6	2	2	27
Mid. and S. Cantby.	13	—	1	4	8	—	15
Otago	8	— ^e	—	3	4	1	13
Southland	17	—	6	6	5	—	21
Totals	71	3	15	26	22	5	Mean 19.5

Davies (1951) proposed a classification of fineness for New Zealand limes into five classes based on percentages retained on two sieves, B.S.S. 16 and 60 mesh. His proposed limiting values are also plotted in Fig. 3. When the curves for the 70 South Island limestones are compared with this two-point standard it is found that only 10 of them are placed in the same class on both counts, 60 of them are placed in a finer category by the 16-mesh than by the 60-mesh criteria, while 31 of these are classed two places finer by the 16-mesh standards. It would seem that, at least for South Island limestones, Davies' 16-mesh limits are set, relatively, too high.

Validity of a Single-Value Classification of Fineness:

The employment of a two-point standard is, of course, an attempt to deal with the fineness curves of more abnormal slope that sometimes occur. However, as already suggested, the results here presented give some grounds for believing that a single-value classification of fineness would be sufficient as a commercial standard. The high correlation between the amounts of > 20 mesh and < 80 mesh material has been mentioned, and it only remains to determine whether that minority of limes whose fineness curves are decidedly abnormal do in fact render a single-value classification unsatisfactory. The fineness curves summarised in Fig. 2 have therefore been analysed with respect to their maximum divergence within each class and the results of this analysis are presented in Table 3 and illustrated in Fig. 4.

TABLE 3. ANALYSIS OF 71 FINENESS CURVES FOR DEVIATION FROM NORMAL SLOPE WITHIN EACH OF FIVE FINENESS CLASSES

Fineness Class	Range of Curves on the Ordinates			(d) Ratio (c)/(b)
	(a) 10 mesh ordinate	(b) 18 mesh ordinate (by definition)	(c) 60 mesh ordinate	
	%	%	%	
Superfine	— —	0.5 = 5	15.49 = 34	6.8
Fine	0.9 = 9	5.14 = 10	18.59 = 41	4.1
Medium	1.11 = 10	15.29 = 15	30.68 = 38	2.5
Coarse	1.17 = 16	30.44 = 15	47.77 = 30	2.0
Very Coarse	12.19 = 7	45+ 3 curves only 48.50 = 2	66.70 = 4	2.0

In Table 3 the range of the curves on the 18 mesh ordinate, shown in Column (b), is, of course, that which defines the fineness class in each case. The full range covered by these same curves on the 10 mesh and 60 mesh ordinates is shown in Columns (a) and (c) respectively. Considering first the divergence of the curves on the 10 mesh ordinate, it is found that the limes containing relatively large amounts of > 10 mesh material are few in number. Thus, 90 per cent of the fine and medium samples hold less than five per cent of that

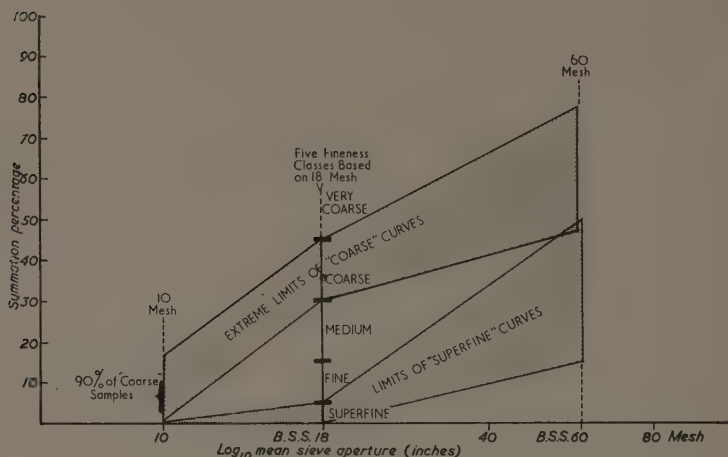


Fig. 4—Analysis of fineness curves of South Island agricultural limes, comparing the maximum deviation from their normal slope of the Coarse and Superfine curves.

material. Moreover, those few samples that contain the larger amounts are confined entirely to the more easily pulverised limes. Turning now to the variability of the curves over the 18-60 mesh interval, the maximum divergence of the curves of each class is expressed by the values of the ratio (c)/(b), given in Table 3, Column (d). The majority of the curves, of course, lie nearer to the mean slope of their class, but it will be seen that the deviation of the abnormal curves is greatest in the case of the superfine curves, and decreases progressively as coarseness increases. This is illustrated for the Superfine and Coarse limes in Fig. 4. Now the point in question is whether this abnormality in the slope of some of the curves is such that it would invalidate the adoption of the proposed single-value standard of fineness. Such would be the case if it were shown that certain abnormal samples were significantly different, in a practical sense, from the more normal samples of their class. It is suggested that the appreciable differences in the degree of fineness that occur in the Fine and Superfine limes (as defined) are of little or no practical consequence. Once a certain degree of fineness is reached the rate of reaction of the lime with the soil and its effects on plants are such that no real advantage is derived from a further increase in fineness. Just where that degree of fineness lies must vary somewhat with the circumstances, and it has not yet been defined, but it seems fairly certain that it lies somewhere within the coarse-sandy range of texture. Walker, for instance, has shown (1952) that arable crops respond to 20-40 mesh limestone applied at normal rates practically as well as to the finer fractions; while the present author has established the great rapidity with which the solubility of these limestones increases once the vicinity of 40 mesh is passed. (Work to be reported in Paper II of this series). It seems clear that any differences likely to occur in the fineness distribution of that portion of the lime finer than 40 mesh (or thereabouts) can be of little practical consequence. It is therefore among the coarser limes that differences in fineness are most important, and the data presented show that the diversity in slope of the coarser

curves is small. It is concluded, therefore, that the variations found to occur in the slope of the fineness curves of the 70 agricultural limes examined are not such as can lead to any error of consequence when their fineness is classified as in Table 2, solely on the basis of the percentages retained on B.S.S. 18 mesh. Whether this would hold for all New Zealand agricultural limes could only be determined by reference to more extensive data.

Wet sieving versus dry sieving

It was noticed that some of the limes, more particularly those derived from low grade shelly limestone, contain particles which are not rock particles but aggregates made up of finer carbonate cemented with earthy impurities. These aggregates, derived it seems from the mud produced in the working of a damp quarry face, and hardened in the kiln-drying process, will slake immediately on wetting, but do not break up on the sieves, with the result that a dry sieving test makes such limes appear coarser than they really are. A similar aggregation has been observed in air-dried samples which had been drawn from damp stockpiles of certain compact limes.

The most satisfactory method found for determining the true fineness of such samples is to water-slake the weighed sample intended for sieving, remove by successive decantations that superfine portion which would include the whole of any clay and silt present, re-dry and dry-sieve the residue. The fraction passing the finest sieve is then determined by difference. Fig. 5 illustrates the extent to which the dry-sieving method may, in extreme cases, give very misleading results. The sample of Limestone f was drawn direct from the bagging hoppers at the works and there was nothing obvious in its appearance to suggest such a degree of aggregation. The results of comparing wet and dry sieving on a series of 38 samples of more or less medium fineness are summarised in Fig. 6, in which the mean curves for compact and shelly limes (equal numbers of each) are shown separately. In the case of the compact limes the difference attributable to wet sieving is small, and at the more important coarse end of the curves appears to be negligible. It is thought

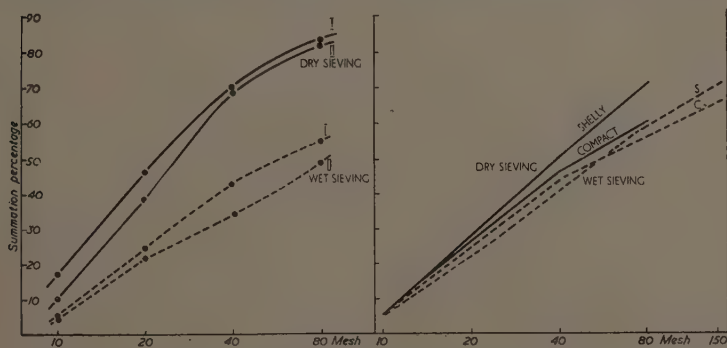


Fig. 5—Extreme examples of aggregation revealed by comparison of dry and wet sieving. I = sample of Limestone N drawn from damp stockpile. II = sample of Limestone f from bagging hopper at works. Fig. 6—Mean fineness curves for shelly and compact limes. The difference is highly significant with both dry and wet sieving.

to be due mainly to the dry adherence of fine dust to coarser particles. A much larger difference results from the wet sieving of the shelly limes. The effect is greatest over the 10-40 mesh range, being due to the breakdown of the coarse aggregates described above, and can obviously lead to appreciable error in assessing the adequacy of grinding of the shelly limes. The difference in aggregation revealed by wet sieving as between the two types of limestone is significant at the 1% level over the whole range of fineness.

Since it must be assumed that wet sieving gives a truer estimate of the size distribution of the limes, it is necessary to consider the bearing of this on the conclusions, already presented, based on dry-sieving data. It appears that a change from dry to wet sieving would make little difference to the general conclusions. The mean fineness curve would be lowered a little, but only by 2% on the 18 mesh ordinate. The range from fine to coarse would be little altered for the reason that more than half the Coarse-to-Very-Coarse samples represented in Fig. 2 are compact limes. The conclusions on the validity of a single-value standard of fineness would, if anything, be fortified, since the divergence of the curves would be less.

Different Crushing Behaviour of Compact and Shelly Limes:

The differences, already noted, in the physical structure of the compact and shelly limestones are not without their influence on the nature of the pulverised products. The difference in aggregation has just been discussed. A further difference is that the compact limes, whether they be hard or soft, yield a higher proportion of fine particles than do the shelly limes. This was first noted when comparing the curves obtained by dry sieving. Most of the shelly limes display a slight upward inflection in the 20-80 range, with consequent smaller pro-

TABLE 4. DIFFERENCES IN FINENESS DISTRIBUTION OF COMPACT AND SHELLY LIMES (19 SAMPLES OF EACH) AS DETERMINED BY DRY AND WET SIEVING

Mesh	Dry Sieving				Wet Sieving				
	10-20 %	20-40 %	40-80 %	< 80 %	10-20 %	20-40 %	40-80 %	80-150 %	< 150 %
<i>Compact Limes</i>									
Means	20.8	18.8	14.5	40.3	20.6	17.9	12.8	9.2	35.0
S.E.	1.21	0.97	0.78	1.58	1.26	0.99	0.81	0.43	1.63
<i>Shelly Limes</i>									
Means	20.7	22.7	20.7	30.0	17.1	18.3	18.6	11.3	30.1
S.E.	1.28	1.06	0.99	1.54	1.42	0.70	0.94	0.45	1.74
<i>Differences</i>									
Compact-Shelly	+0.1	-3.9	-6.2	+10.3	+3.5	-0.4	-5.8	-2.1	+4.9
t	—	2.71	4.91	4.66	1.84	—	4.68	3.38	2.08
Level of Significance	—	1%	1%	1%	n.s.	n.s.	1%	1%	5%

portion of really fine material. This difference between the mean curves for shelly and compact limes (the unbroken lines Fig. 6) proved to be highly significant. It was thought at first that the difference was due to the greater aggregation of the shelly limes. However, correction of these curves to true fineness by wet sieving (see broken lines in Fig. 6) was found to reduce but not to eliminate the significant difference between the two types. Over the range 40-150 mesh this difference remained significant at the 1% level, and is denoted in Fig. 6 by the difference in the slope of the mean curves, marked C and S. The relevant data are presented in Table 4. It is evident that the difference in fineness distribution resulting from the crushing of the two types of lime, though small, is a characteristic one. It is the more remarkable in view of the fact that the compact limes included in this comparison ranged from the hardest to the softest limestones.

As to the cause of this difference, it is surmised that the shelly limes, derived from shell sand bonded to a greater or lesser degree by recrystallised calcite, disintegrate more readily under the beat of the hammers (the hammer-mill being the type of pulveriser usually employed) into fragments which are of a size that can readily escape through the screen. In some cases it is clear that these fragments are the original shell sand components of which the limestone was made. The compact limes, it is suggested, being more homogeneous in structure, shatter into fragments possessing a more normal gradation in size, which therefore require more impact from the hammers before all are reduced to sub-screen dimensions. The inevitable result is a greater proportion of fine and ultra fine particles. Supporting evidence for this explanation is found in the fact that, among those which have been closely studied under the microscope, it is the compact limes whose coarser particles are noticeably abraded at the edges.

Deceptive Appearance of Fineness: One consequence of the difference in aggregation and crushing behaviour of the two types of limestone is that compact limes appear to the eye to be much more finely ground than do shelly limes of equal fineness. On visually inspecting a sample contained in a glass jar, one receives an impression of coarseness or fineness which is chiefly determined by the degree to which the spaces between the coarse particles are infilled with finer material. It was at first thought that this might provide a useful practical guide as to whether or not adequate comminution had been achieved; but Fig. 7 shows how misleading appearances can be. When visual appearance of fineness, classified on a 12-point scale, is plotted against percentage retained on B.S.S. 18 mesh, the compact and the shelly limestones fall into two distinct groups, within each of which there is an obvious correlation between the co-ordinates, but between which there is a marked division. The shelly limes appear much coarser than the compact limes. The distinction is well illustrated by the two limes marked p and q in Fig. 7. Sample p is derived from a soft chalky fine grained stone, and is coarsely crushed, containing 39% coarser than B.S.S. 18. To the eye, however, it appears finely ground. Sample q, on the other hand, is a well pulverised shelly lime, containing only 22% coarser than B.S.S. 18; yet it appears to be excessively coarse. The explanation lies in the greater amounts of really fine material, particularly that finer than 150 mesh, that is present in the samples derived from

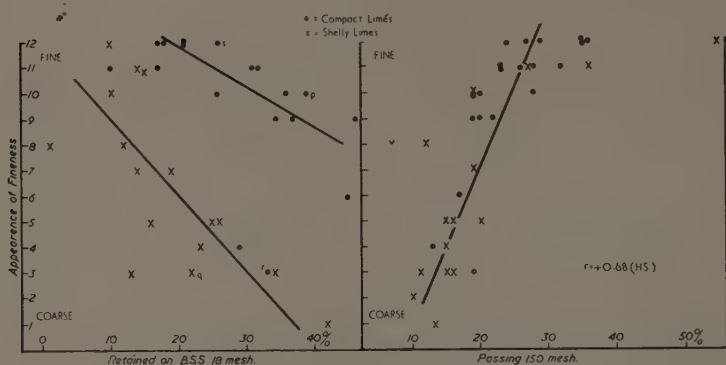


Fig. 7—Appearance of fineness compared with sieve grading on B.S.S. 18. Compact limes appear finer.

Fig. 8—Appearance of fineness shown to be governed by the percentage of < 150 mesh material.

compact limestones. Thus, the coarser sample p is given the appearance of fineness by virtue of its content of 28 per cent of < 150 mesh material; while the finer sample q appears coarse because it contains only 15% of < 150 mesh material. This misleading influence of the finest fraction on the appearance of fineness is established in Fig. 8 where the appearance of fineness is plotted against percentage of material < 150 mesh. The separation of the two types of lime now disappears and a high over-all correlation takes its place. This effect of the finest material is presumably due to its loose packing and fluffy nature. It is of course being assumed that fineness in terms of the 18 mesh sieve is of far greater practical significance than fineness in terms of the 150 mesh sieve. Evidence in support of this assumption has already been referred to.

Exceptional cases are the two compact limes which fall into the camp of the shelly limes, one of whose plots is marked r in Fig. 7, the other being nearby. The latter is not easily accounted for, but Sample r, on closer examination, is found to confirm the rule. This lime has a counterpart, from the same quarry but of different date, which falls properly within the compact group, marked s in Fig. 7. Careful comparison of Samples r and s shows that both are derived from shell fragments, but in Sample s, and other samples received from this quarry, the stone has been so thoroughly hardened and compacted by recrystallization that it has conformed to the compact type and been classified accordingly. Sample r, however, is much less compacted by recrystallization and is honeycombed with cavities, mostly of organic origin. Its appearance classes it as a shelly lime, and in fact it has behaved as such on crushing.

Moisture Content

The moisture content of the pulverised lime as marketed has importance in that if allowed to become too high it will result in impeded flow and bridging of the lime in storage hoppers and spreaders, and will effect a proportionate reduction in the carbonate content. The limestones examined vary considerably both in the moisture contents

of the freshly quarried stone and in their capacity to absorb additional moisture from rain. Some of the denser stones are so impervious that wet rock can safely be crushed and yield a dry product; but the majority of the limestones are porous enough to hold undesirable quantities of moisture. Most of the larger limeworks therefore find that to ensure continuous production throughout the year it is necessary to kiln-dry the pre-crushed stone before it passes through the pulveriser. There are, on the other hand, wide variations in the moisture contents that are acceptable in different limes. The very dense limes, by holding moisture almost solely on their external surfaces require very little moisture to make them damp and difficult to sow. In one such instance 4% of moisture was sufficient to cause difficulties in the spreading, whereas a softer somewhat chalky lime was found to hold as much as 10.5% of moisture and still behave well in the normal type of spreader. There is therefore no uniform standard governing moisture content. Economy of production and ability to spread freely are the sole controlling factors.

Owing to the fact that the pulverised samples were not obtained in air-tight containers, the moisture content of the limes, as marketed, could not in most cases be determined. However, a dozen or so reliable values obtained for bagged lime range from 1.8% for a hard crystalline lime up to 9.3% for an undried soft chalky lime (percentages of the oven-dried weight). Comparison with the values for equilibrium moisture content, listed in Table 7, Column 6, shows that these samples were considerably moister than when air-dried. Undried lime delivered direct from the quarry in bulk-spreaders has more recently been found to contain up to 13% of moisture, while damp lime drawn from open-air stockpiles has been satisfactorily spread while containing from 14 to 16%, and on one occasion as much as 20% of moisture, by bulk-spreading machines suited to this purpose. Since the development of open-air stockpiling, samples are occasionally received in a very moist condition. Since such limes are no longer measured and sold by weight but in effect by volume, there is no point in allowing their highly variable moisture contents to enter into the reckoning of their purity, and the convention has been adopted of allowing such limes to become air-dry before analysis.

Equilibrium Moisture Content

It was anticipated that the total specific surface, internal and external, of the crushed limestone particles might be closely related to their rate of solution in the soil. Data on the relative specific surface of the 10-20-sieve fractions of the different limes were therefore obtained by measuring their adsorption of water at a relative humidity of 86.5% by holding over saturated potassium chloride solution in a constant temperature room (19-20°C.)

The equilibrium moisture contents range widely from the extremely low value of 0.02% for the dense finely crystalline stone Y, up to the abnormally high values of 3.4 and 4.5% for the two nearby deposits J and K in North Canterbury. (Table 7, Column 6.) The values are significant characteristics of the different limestones, the factor for significant difference between any pair of means (5% level) being

$\times 1.094$. Thus limestones B and U are significantly different in their equilibrium moisture contents, but limestones B and A are not. However, these values display a negative correlation coefficient of -0.74 with the carbonate content of the materials tested, and it is clear that it is not the calcite surface but that of the non-calcareous impurities that dominates moisture adsorption. Pure calcite evidently has a very low equilibrium moisture content (see limestone C), and it is concluded that this property can have no bearing on the rate of solution of the different limes.

Porosity

It was obvious from the most superficial inspection that the porosity of the limestones varies to an extreme degree, and that this must play a major part in determining the hardness of the stone, and the physical characteristics of the crushed product. Porosity determinations were therefore made on four typical pieces, of not less than 25 g. each, of the stone obtained from each of the quarries. The method recommended by Hillebrand and Lundell (1929) was employed. After removal of surface irregularities and loose fragments, the pieces were oven-dried, weighed and placed in a desiccator evacuated to a pressure of < 10 mm. of mercury. Cold boiled water was admitted till it just touched the stones. After several hours, more water was very slowly admitted till the stones were completely submerged and saturated. After temperature adjustment to 20°C ., they were weighed suspended in water, then wiped free of superficial moisture and weighed (saturated) in air. This method enables the true specific gravity as well as the apparent specific gravity and porosity to be calculated. The mean value obtained for specific gravity was 2.711, with a standard error of only ± 0.002 , and the constancy of the values obtained is evidence of the accuracy of the determinations. The specific gravity of calcite at 25°C . is 2.711.

The visual impression of an extreme range in porosity is confirmed. The mean values obtained (Table 7, Column 7) range from 0.6 to 48.8%. In view of the fact that representation of major variations in the rock at each quarry was purposely sought when taking the samples, it is surprising how consistent most of the quadruplicate tests are. The factor for significant difference between any pair of means (5% level) is approximately $\times 1.3$. Thus the porosity means for limestones H and I are significantly different. It is clear that the porosity values obtained are significant characteristics of the different limestones.

These data, however, do not reveal one important difference, namely, the difference in the texture of the porosity. In the case of the compact limes, whose porosity is fine textured, the finer splinters may be as porous as the coarsest particles; whereas the porosity of the shelly limes, being coarse textured, tends to disappear as the fragments break down to their component splinters of shell and secondary calcite. This is well illustrated by the comparison between the crushing behaviour of limestones N and T, illustrated by the first four plates of Fig. 1. Both limestones are highly porous but very different in texture. Their mean porosities are 24.9 and 37.3% respectively. Plates A and B show the 20-40 and 80-150 mesh fractions of the compact chalky limestone N. The particles of the two fractions appear identical except in size, the smaller ones retaining all the lightness and porosity of the massive stone.

A higher magnification shows them to be honeycombed with minute cavities. In sharp contrast is the effect of crushing on the shelly limestone T, illustrated by Plates C and D. The coarsely porous highly irregular 20-40 mesh particles consisting of loosely bonded fragments of shell, quartz and glauconite, fall apart into the much more uniform and dense 80-150 mesh fragments seen in Plate D. Some measure of this effect is also given by the relative numbers of particles (Equivalent Centres) yielded by limestones P and U. (Table 7, Column 13). Though virtually equal in their high porosity, the particles of the fine grained chalk retain the whole of their porosity, are low in density and correspondingly more numerous per equivalent of calcium, than are those of the coarsely porous shelly lime U. The significance of this residual porosity of the particles will become more apparent later.

When the study of the above described properties had been completed, a selection was made of 24 limestones judged to include all evident variations of likely significance, with a view to the subsequent comparison of their rates of solution in the soil. The further observations on physical properties, reported below, were confined to these 24 limes.

Grindability

In the absence of other convenient means of measuring the hardness or crushing stress of the limestones, a series of empirical observations on the relative grindability of the 10-20 mesh fractions was made. This material has the advantage of being much more representative than are a few larger pieces of stone. According to the Rittinger Law (Gross, 1938), the work done in the crushing of any material is directly proportional to the amount of new surface produced. The relative grindability of a material has therefore been defined as the work necessary to produce a given amount of new surface, and a standard run in a ball-mill has commonly been employed for making comparisons of grindability on the assumption that a constant amount of work is then done on the material. (DallaValle, 1948). In adopting this procedure, it was planned, to measure the resultant increase in specific surface by means of the surface reaction with N/10 oxalic acid, described in a succeeding paragraph. Difficulties were encountered, however, in applying this method to the flourey material produced in the mill and, moreover, it was shown that the amount of new surface possessed by the < 80 fraction was so incomparably greater than that of all the coarser products of crushing that valid comparisons of grindability could be made simply in terms of the percentage of < 80-mesh material produced. The principle of this is in accordance with an accepted A.S.T.M. method for measuring the grindability of coals. A run of twenty minutes in a small porcelain ball-mill on a standard charge of dry water-washed 10-20 mesh limestone was found suitable for the range of hardness involved, and resulted in a mean reduction to 38 per cent of < 80-mesh material. It would be more orthodox to express grindability in terms of the work done, or mill revolutions needed, to effect a standard reduction in size. The values so obtained, however, display a hyperbolic relationship with other properties, and the results have therefore been reported in terms of percentage reduction to < 80 mesh, which values approximate to a linear relation with other characters. (See Table 5.)

The values obtained (Table 7, Column 8), range from 7.6 per cent for the very hard flinty limestone H, up to 80.6 per cent for the soft shelly lime Q. The value for the chalk P is unreliable, since the whole of this exceptionally soft chalk was reduced to < 80 mesh. It is interesting to note that the two limestones which, judging from their appearance and porosity might be taken as two of the hardest, Sample C, the white marble, and Y, a palaeozoic unusually dense flinty looking stone, are by no means the most difficult to grind. The white marble is surprisingly easy to crush and its highly pure rather coarsely crystalline calcite is far more brittle than other stones of lower purity and higher porosity.

Other Physical Properties

The remaining simple observations on physical properties require little explanation, though their connection with the equivalent calcite surface of the different limes is considerable. Some interesting relationships are discussed in a following section.

Irregularity of particle shape obviously affects surface area. The irregularity of the 20-40-mesh particles of the limes as seen through a low power stereoscopic microscope was graded on an arbitrary scale in which an attempt was made to assess the extent to which the shape of the particles and their surface irregularity contributed to a greater surface area, over and above the effects due to porosity. The indices ranged from 1.1 to 1.8, and are listed in Table 7, Column 15. The two limes N and T, shown in Fig. 1, were graded 1.3 and 1.7 respectively.

The numbers of centres per unit weight of CaCO_3 (20-40-mesh separates), listed in Table 7, Column 13, as "Equivalent Centres", reflect the combined influence of the widely varying values for purity, porosity, shape and irregularity of the particles. As shown later, these characteristics appear to be summed up to a remarkable degree in the simple measure of Apparent Volume per gramme CaCO_3 , of the 20-40-mesh separates. (Table 7, Column 14). This was determined by observing the gross volumes of equivalent weights of the different separates after pouring into a measuring cylinder under standard conditions.

PHYSICO-CHEMICAL PROPERTIES

Reactivity Index

Davies' improvement (1949) of Jones's method (1941) for determining indices of reactivity for the different limestones has been referred to. The method aims to compare chemically equivalent portions of a standard sieve fraction of the various limes in terms of their rates of solution in partially neutralised acetic acid. Davies most kindly offered to measure the reactivities of the 24 limes destined for rate of solution studies, and for purposes of comparison his results are included, with due acknowledgement and thanks, in Table 7, Column 9. According to Davies (1948) the test was carried out on the 16-30 B.S.S. sieve fraction which was agitated in a buffered acetic acid solution of pH 2.9, held at constant temperature. The index reported is the increase in conductivity in reciprocal ohms $\times 10^3$ between 30 sec. and 50 sec. from the start of the reaction. The higher indices thus correspond to the more reactive limes. During this short period, the rate of reaction is

stated to be fairly constant and conductivity proportional to the amount of calcium dissolved.

The values recorded are somewhat higher than corresponding values published by Davies, since the sieve fraction used was a little finer. The range of values, however is comparable, running from 22 for the white marble C, up 72 for the soft shelly South Canterbury lime, T. One exception is the abnormally reactive chalk P, whose solution was so rapid that the reaction had slowed down before conductivity measurements commenced. Even so, an index of 190+ was recorded.

Surface Reaction with Oxalic Acid

A method was described by Barnes (1947) for comparing the relative surfaces of liming materials and other feebly soluble calcium salts. His procedure was to steep clean washed sieve separates in saturated oxalic acid solution for one and a quarter hours, and then determine the calcium oxalate formed. It was suggested that the film of calcium formed will have brought the reaction nearly to a stop. This procedure suggested the possibility of a very simple means of comparing the calcite surfaces of the lime separates.

Preliminary trials revealed large differences in the rates of reaction of the different limes, but the reaction showed no signs of terminating. In the case of some soft and fine samples (80-150 mesh) the reaction was vigorous enough to cause feeble effervescence, and as much as 85% of the carbonate had reacted in 24 hr. It was clear that this was not a surface reaction of the type required. However, further experiment using N/10 oxalic acid, revealed that there was in fact an extremely rapid initial reaction with the readily accessible calcite surface, which was 80% completed or more during the first 5 sec. and almost fully completed within 30 sec. and that this was followed by a very much slower and protracted secondary reaction. The latter is presumably concerned more with the internal than the external surfaces since it displays a high correlation with both porosity and grindability. (Table 5.)

The method adopted was as follows. Chemically equivalent weights of the order of one gram of the thoroughly washed and dried sieve fractions were employed. Each was placed in a Gooch filter, the flask of which was connected via a stop-cock to a second large vacuum flask and pump. Twenty ml. of N/10 oxalic acid were added to the lime and the rate of filtering adjusted by manipulation of the stop-cock to permit the carefully timed period of contact, at the expiry of which the lime was quickly washed with hot water. Contact periods of 5, 15 and 30 sec., 1½ min. and 3 min. were found suitable. The contents of the filter were digested for one hour in 150 ml. of hot 10% sulphuric acid, and titrated with N/10 KMnO_4 . The speed of the reaction between oxalic acid and lime was not particularly sensitive to change of temperature, and adjustment of the temperature of the oxalic acid solution before applying it to the lime proved all that was necessary. Fig. 9 gives three typical reaction curves. Limestone T, highly porous and friable, is the most reactive lime, with the exception of the chalk, and Limestone C, the white marble, the least reactive. The virtual absence

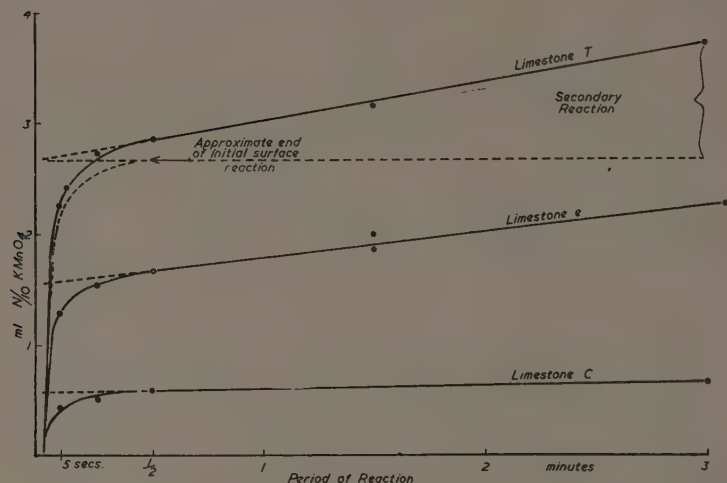


Fig. 9.—Typical reactions of limestones (20-40 mesh) with N/10 oxalic acid. The initial surface reaction is taken as a measure of equivalent calcite surface.

of any secondary reaction in the latter case, due to the impervious nature of this stone, is in marked contrast to the vigorous continuation of the reaction with the soft porous limes. About 1½% of Limestone T had reacted with the oxalic acid in the period of three minutes. All limes gave curves of similar form, with the exception of the chalk, with which the initial reaction continued for about one minute. In interpreting the results it was presumed that the slower secondary reaction had been taking place from the beginning and that the curve for the first half minute expressed the sum of the two reactions. The end of the initial reaction was therefore extrapolated by projecting the straight line of the secondary reaction backwards to zero time. The second reaction was recorded in terms of its extent up to the end of the third minute, it having been established that its rate declined very gradually from then on. The reactions are listed in Table 7, Columns 11 and 12, as milliequivalents per cent.

Both the initial and the secondary reaction display a high correlation with porosity and with each other (see Table 5) and it is surmised that there is nothing fundamentally different or discontinuous between the two, but that both are reflections of the varying amounts of calcite surface per unit weight of CaCO_3 resulting from differences in porosity, purity and irregularity of particle shape. The immediate rapid reaction with the external surfaces is quickly slowed down during the first half minute, presumably by the precipitated layer of calcium oxalate; but not altogether stopped, it would seem, for even the densest of the stones, Y, with little if any internal surface, maintains a steady though extremely slow continuation of the reaction, with no sign of cessation after 24 hr. The much larger secondary reaction of the more porous limes must therefore be due mainly to their considerable internal surfaces. When observations were extended over much longer periods

the reaction appeared to continue unchecked towards a state of complete reaction, though at steadily diminishing rates. The initial reaction is accepted as a direct measure of the external Equivalent Calcite Surface of the tested sieve fractions. Its relationship with actual surface area has not been determined, but proportionality between the two has been assumed. It has also been assumed that all CaCO_3 , other than that small amount which may be combined with Mg as dolomite, is present in the form of calcite. No evidence of aragonite was found in the few samples tested with cobalt nitrate.

The relationship between equivalent calcite surface, thus determined, and other properties is discussed below. Compared with the Reactivity Indices as determined by Davies, its values, ranging from 4.7 to 21.4 m.e. %, make a 50% wider separation of the limes; and although two-thirds of them are placed in approximately the same order by both methods, there remain some very marked and unaccountable anomalies. The correlation co-efficient between the two assessments of calcite surface is 0.835.

EQUIVALENT CALCITE SURFACE

The main purpose in conducting the above series of observations on the physical properties of the limestones was to determine whether any one property or group of properties might be found which would correlate sufficiently with the rates of solution in the soil to serve as a practical guide to the availability of the calcium in the wide variety of agricultural limes used in New Zealand and elsewhere. The actual differences in solubility in the soil are reported in the succeeding paper of this series. There are, however, some significant relationships among the properties measured which bear closely on the question of solubility.

It is probably correct to assume that the greatest single factor governing solubility of limestone in the soil is the total external calcite surface of the particles per unit weight of CaCO_3 , referred to already as the equivalent calcite surface. Fineness of grinding must obviously play the major part in determining this, but since attention at the moment is directed to differences between limestones, fineness will be assumed as constant, and the influence of the inherent properties of the limes will be considered. For any series of comparable sieve separates, such as the 20-40-mesh separates reported on above, the equivalent calcite surface of each lime must be largely determined by four characteristics: the purity, porosity, general shape, and surface irregularity of the particles. The influence of purity in this respect was noted by Salter and Schollenberger, (1940). Impurities and pore spaces both exert a diluting or distending effect which results in unit weight of carbonate occupying widely different volumes in the different limes. Taking pure calcite of nil porosity as 100, the values for the Equivalent Volume were calculated from the purity of the 20-40 mesh separates and the porosity data using the formula.

$$\text{Equivalent Volume} = \frac{100}{\text{purity}} \times \frac{100}{(100 - \text{porosity})}$$

The values obtained (Table 7, Column 16) range from 103 for the highly pure Marble C. of very low porosity, up to 229 for the highly

porous and only moderately pure Chalk P. Supposing these two limes could be broken into identical sieve separates, ideal in their uniform particle shape and perfect size distribution, the number of particles or centres produced per equivalent of calcium, and therefore their respective values for equivalent calcite surface, would be in the same ratio of 103:229, except insofar as impurities might be exerting a shielding effect. Purity and porosity, individually and together, must therefore exert a major influence in determining equivalent calcite surface. This is substantiated by the correlation co-efficients recorded in Table 5. Purity and porosity achieve co-efficients of -0.643 and 0.654 respectively with equivalent calcite surface as measured by the initial oxalic acid reaction, while their combination as equivalent volume displays the higher correlation of 0.832 .

Another factor must now be considered, namely, the shape and surface irregularity of the particles. If these were uniform in shape, the number of centres per unit of CaCO_3 (equivalent centres) would be directly proportional to the equivalent volumes. Such proportionality, however, does not exist. The ratio between the two varies widely, and this is an indication of the variability in particle shape. The form of the particles varies from lime to lime in the following ways: the shapes approximate variously to cuboid, prismatic, cylindrical, platy and splintery forms; the edges vary from obtuse and rounded to sharply acute; while the surfaces may be plane and smooth, irregular, pitted, fluted or honeycombed, and in some cases noticeably shielded by grains of non-calcareous impurities, such as glauconite and haematite. Some of these features will be noticed in Fig. 1. A moment's consideration of the passage of such diversely formed fragments through the apertures of a sieve will make it obvious that the mean volume per particle, and hence the number of particles and total surface per unit weight, must vary considerably from lime to lime. Thin flat splinters, for instance, may have several times the specific surface possessed by more cuboid particles of the same maximum dimensions. The counts of equivalent centres, however, do not measure this irregularity, since they are governed by purity and porosity as well as irregularity. The Irregularity Indices were therefore recorded with a view to assessing, so far as visual observation could do, the extent to which specific surface was increased by virtue of the variations in form. The predicted relative values for equivalent calcite surface listed in Table 7, Column 17, were then obtained as the products of the respective equivalent volumes and irregularity indices. In Fig. 10 they are compared with the experimental values of that function, derived from the oxalic acid reaction. With two exceptions (Limestone A and Chalk P) the prediction has been remarkably accurate in the case of the compact limes. The rather more erratic predictions in the case of the shelly limes is doubtless connected with the facts that the porosity data employed do not apply to the hard shell fragments of which these limes are composed, and that some of that porosity is lost on crushing. The improvement in the prediction resulting from the inclusion of particle irregularity is not great, and it is clear that purity and porosity are the major factors determining equivalent calcite surface.

It seems that the widely differing values of purity, porosity and irregularity of the different limes, as they combine to affect the number of centres and equivalent calcite surface, are summed up with surprising

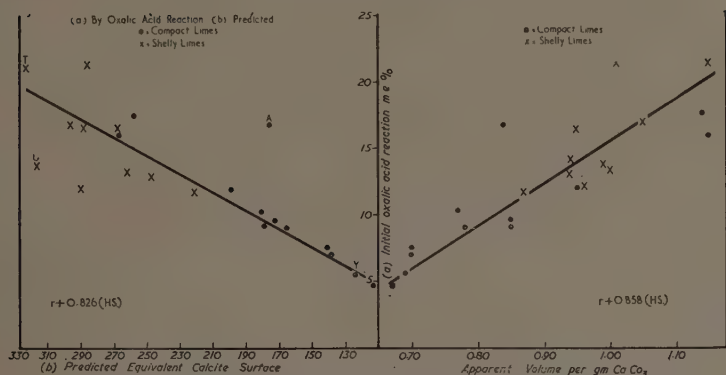


Fig. 10—Equivalent calcite surface of limestones (20-40 mesh)

(a) measured by oxalic acid reaction
(b) predicted. (Equivalent Volume $\times$ Irregularity Index)

Fig. 11—Equivalent calcite surface compared with apparent volume of 20-40 mesh separates.

accuracy by the simple measure of the apparent volume of the loose packed equivalent weights of the 20-40-mesh separates. (Fig 11.). This function displays a correlation co-efficient of 0.953 with the equivalent calcite surface as experimentally determined and, as will be shown in the succeeding paper, shows a similar correlation of 0.944 with the measured rates of solution of the limes in the soil. The correlations shown in Fig. 10 and 11 are calculated with the exclusion of the Chalk P, for which abnormal material the prediction of equivalent surface was completely astray.

GENERAL RELATIONSHIPS BETWEEN THE PROPERTIES

A noticeable feature of the results is the close inter-relationship which exists in the majority of cases between the properties measured. The correlation coefficients, displayed by various pairs of these properties are shown in Table 5, the values for the chalk being included in every case. All but one of these coefficients are well above the level required for one per cent significance. It is obvious that significant correlations must of necessity exist between other pairs. Such a close inter-relationship it not, after all, surprising in view of the established influence of purity and porosity on the various functions of surface, and the obvious connection between porosity and grindability.

The consequence is that the equivalent calcite surface (as measured by the oxalic acid reaction) holds a significant relationship with most of the other characteristics. Its negative correlation with purity is not due to the more impure limes being softer, since there are too many exceptions to allow this tendency to be regarded as a rule. (See in Table 5, the low correlation between purity and grindability). The negative correlation with purity is due, as shown above, to the greater dispersal of an equivalent weight of the less pure limes, when taken at the same fineness. The secondary reaction with oxalic acid is seen to be rather more closely related to porosity and grindability than is the initial reaction, supporting the view, previously expressed, that the secondary reaction is chiefly concerned with the internal surfaces. The

TABLE 5. CORRELATION COEFFICIENTS BETWEEN CHARACTERISTICS OF 24 LIMESTONES

	Equivalent Calcite Surface (per reaction with Oxalic Acid)	Porosity	Grindability	Equivalent Volume (Calculated)
Secondary Reaction with Oxalic Acid	0.845	0.839	0.846	0.950
Reactivity Index	0.835			
Purity	-0.643		-0.285	
Porosity	0.654		0.736	
Grindability	0.713			
Equivalent Volume	0.823			
Equivalent Calcite Surface (predicted)	0.735*			
Apparent Volume (Measured)	0.953			

Level for 1% significance = 0.526

* Including chalk P

high correlations between the three functions, equivalent calcite surface (measured), equivalent volume (calculated) and apparent volume (measured) confirms the conclusion that the differences in the shape and irregularity of the particles play a comparatively minor role in determining the degree of dispersal and equivalent calcite surface of the different limes.

The course of the relationships is strikingly illustrated if two strongly contrasting limes are considered. Let us consider first the properties of the extremely hard limestone Y: its high purity, extremely low porosity and smooth rotund particle shape combine to give it abnormally low values for equivalent volume, equivalent centres, apparent volume and for its reactions, both initial and secondary, with oxalic acid. In contrast to this, Limestone T, with its low purity, high porosity and irregularity (See Fig. 1) occupies one of the highest positions in respect of all the other characteristics mentioned. The positions of these two limes are indicated in Fig. 10.

There are a few notable exceptions to this general trend. The dense finely crystalline stone A, of unusually low purity for this type of stone, is abnormally high in its chemical reactivity with oxalic acid. (Fig. 10). No explanation of this has been found. On the other hand, the coarsely porous shelly lime U is less reactive with oxalic acid than its equivalent volume and irregularity would suggest; but this is accountable by the fact that much of its coarse porosity must be lost in the crushing process. Other anomalies occur in respect to the ease of grinding of the limestones. Although grindability and porosity are highly correlated (0.736) the two limestones of lowest porosity and highest purity (C and Y) have the unexpectedly high grindability values of 38.7 and 19.0 respectively. In contrast to these are six limes whose porosities are higher and purities lower by a considerable margin, but

TABLE 6. COMPARISON OF PROPERTIES OF COMPACT AND SHELLY LIMESTONES

	% Purity of Commercial Samples	% MgO	% P ₂ O ₅	% Purity of 20-40 separates	% Beneficiation of 20-40 separates	% Porosity	Grindability	Equivalent Calcite Surface (per oxalic acid reaction) m.e. %	Secondary Reaction with Oxalic acid m.e. %	Equivalent Centres 10 ³	Apparent Volume ml.	Irregularity Index	Equivalent Volume	Predicted Relative Equivalent Calcite Surface
<i>Compact Limes</i>														
Means	86.9	0.38	0.30	89.0	2.60	10.7	24.8	10.4	2.95	4.70	0.84	1.4	129	176
S.E.	3.02	0.059	0.088	2.72	0.40	2.71	4.57	1.24	0.54	0.33	0.048	0.039	7.4	13.7
<i>Shelly Limes</i>														
Means	79.4	0.71	0.20	89.9	10.54	32.1	46.4	15.4	6.05	5.22	0.99	1.7	166	280
S.E.	3.42	0.102	0.063	1.90	2.20	2.25	6.58	1.13	0.49	0.27	0.024	0.028	6.0	9.7
<i>Differences</i> (Shelly-Compact)	-7.5	+0.33	-0.10	+0.9	+7.94	+21.4	+21.6	+5.0	+3.1	+0.52	+0.15	+0.3	+37	+104
t	1.65	2.80	0.92	0.27	3.66	6.10	2.70	2.99	4.28	1.18	2.81	6.25	3.90	6.20
Significance	n.s.	2%	n.s.	n.s.	1%	1%	2%	1%	1%	n.s.	2%	1%	1%	1%

TABLE 7. CHEMICAL AND PHYSICAL PROPERTIES OF 32 SOUTH ISLAND AGRICULTURAL LIMESTONES

Designation		Commercial Crushed Samples										20-40 Mesh Separates									
		Bases as CaCO_3		Acid soluble				$\text{CaCO}_3 + \text{MgCO}_3$ (as CaCO_3)	Equilibrium Moisture (content)	Mean Porosity	Grindability Reduction to > 80 mesh	Reactivity Index	CaCO_3 Equivalent	Equivalent Calcite Surface (by Oxalic acid Reaction)	Secondary Reaction with Oxalic acid	Equivalent Centres	Apparent Volume per g CaCO_3	Irregularity Index	Equivalent Volume	Predicted Relative Equivalent Calcite Surface	
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17			
		%	%	%	%	%	%	%	%	%	%	%	m.e. %	%	10^6	ml.	1.1-1.8				
NELSON																					
A	Compact hard grey finely crystalline	78.1	42.2	0.90	0.14	77.5	0.16	2.3	18.2	27	81.1	16.7	3.5	5.0	0.84	1.4	126	176	A		
B	Compact hard grey-brown some shell fragments	92.8	51.4	0.68	0.06	93.5	0.15	2.8											B		
C	Compact very hard white marble	98.3	54.3	0.33	0.11	97.7	0.04	1.2	38.7	22	97.8	4.7	0.5	4.7	0.67	1.1	103	113	C		
D	Compact very hard white fine grain	94.0	52.8	0.27	0.12	94.9	0.07	4.0	8.9	34	95.4	7.5	2.1	3.5	0.70	1.3	109	142	D		
E	Compact very hard white medium grain	93.2	51.5	0.28	0.15	92.6	0.23	2.0											E		
MARLBOROUGH																					
F	Compact very hard cream almost flinty	88.4	49.2	0.21	0.30	88.3	0.99	8.9											F		
G	Compact hard white-grey fine grain almost flinty	88.8	49.1	0.21	0.65	88.6	0.63	8.2	12.8	34	90.4	10.2	3.1	4.3	0.77	1.5	121	181	G		
H	Compact very hard white very fine grain flinty	76.7	42.0	0.24	0.12	75.6	0.97	6.1	7.6	32	79.8	9.5	3.0	4.9	0.85	1.3	133	173	H		
I	Compact hard white-grey fine grain	77.5	42.8	0.25	0.09	76.9	1.34	8.0											I		
N. CANTERBURY																					
J	Compact hard white-grey fine grain	74.7	41.8	0.28	0.22	75.3	4.48	33.7											J		
K	Compact hard white-grey fine grain	69.6	39.2	0.27	0.19	70.7	3.41	21.0	33.4	42	71.3	15.9	6.1	6.6	1.15	1.5	178	267	K		
L	Compact very hard grey-brown coarsely crystalline	96.3	53.5	0.53	0.53	96.8	—	3.7	14.5	27	97.0	7.0	0.7	3.5	0.70	1.3	107	139	L		
M	Compact mod. hard cream-grey medium grain	72.7	41.5	0.39	1.08	75.0	1.49	25.1	62.7	51	77.6	17.6	5.6	6.9	1.14	1.5	172	258	M		

	78.7	43.7	0.22	0.31	78.5	1.49	24.9	35.5	42	86.8*	11.9	5.0	4.2	0.95	1.3	153	199	N
white very fine grain chalky																		
O Compact mod. hard	76.2	43.3	0.19	0.23	77.8	1.70	—	46.4	53	77.2	15.5	4.3	6.7	1.05	1.5	—	—	O
P Compact very soft white chalk	77.8	—	—	—	—	2.11	45.9	100	109	80.9	44.0	12.6	7.9	1.39	1.5	229	343	P
MID. & S. CANTERBURY																		
Q Shelly mod. soft cream sandy grain	86.3	48.0	0.86	0.25	87.8	—	28.9	80.6	51	91.2	13.3	8.3	4.0	1.00	1.7	154	262	Q
R Compact hard cream med. grain semi-crystalline	93.4	51.2	0.51	0.10	92.7	0.35	13.1	17.6	39	97.1	9.0	2.1	4.9	0.78	1.4	119	166	R
S Shelly mod. hard cream grey sandy grain Glau- conitic	61.1	34.9	0.54	0.69	63.6	2.11	19.6											S
T Shelly soft cream-grey sandy grain Glauconitic	74.1	39.9	0.74	0.69	73.0	0.74	37.3	77.0	72	83.2	21.3	8.1	6.4	1.15	1.7	191	323	T
OTAGO																		
U Shelly soft cream-white coarse grain	96.3	54.0	0.46	0.14	97.4	0.13	48.8	62.5	60	98.5	13.8	7.8	4.4	0.99	1.6	198	316	U
V Shelly soft cream-yellow coarse grain	79.8	43.5	0.90	0.11	79.8	2.53	37.2											V
W Compact very hard white fine grain semi-crystalline	91.7	50.9	0.50	0.25	92.1	0.27	18.4	28.2	57	96.0	9.0	2.7	5.1	0.85	1.4	128	179	W
Y Compact very hard grey finely cryst. almost flinty	96.5	53.2	0.18	0.10	95.4	0.02	0.6	19.0	30	97.4	5.6	1.0	2.8	0.69	1.2	103	124	Y
SOUTHLAND																		
a Shelly soft cream-brown sandy grain Glauconitic	74.9	40.8	0.76	0.07	74.7	1.13	29.0	56.7	54	80.8	16.9	6.1	6.5	1.05	1.7	174	296	a
b Shelly mod. hard cream- yellow coarse grain	80.9	45.3	0.46	0.13	81.9	0.63	24.0	28.3	52	94.5*	11.7	3.7	5.1	0.87	1.6	139	222	b
c Shelly mod. hard cream- grey medium grain	71.2	38.6	1.47	0.18	72.6	0.82	31.3											c
d Shelly mod. hard grey- brown coarse grain Glau- conitic	61.3	33.4	1.15	0.15	62.4	1.16	32.3	30.7	44	82.4	21.4	5.3	5.9	1.01	1.6	179	286	d
e Shelly mod. hard cream- brown coarse grain Glau- conitic	84.7	46.1	0.90	0.13	84.4	0.83	31.0	27.5	56	90.1*	12.1	6.1	4.4	0.96	1.8	161	290	e
f Shelly mod. hard cream coarse grain Glauconitic	57.9	31.7	0.93	0.11	58.9	1.07	24.5	33.4	54	89.1	16.4	5.2	5.5	0.95	1.8	149	268	f
g Shelly mod. soft cream- yellow coarse grain Glau- conitic	89.0	49.3	0.15	0.13	88.4	0.45	34.5	34.8	58	95.5	14.1	5.0	5.3	0.94	1.8	160	288	g
h Shelly mod. soft cream- yellow medium grain	82.7	—	—	—	—	—	31.1	32.6	50	93.9	13.0	3.1	4.7	0.94	1.6	155	248	h

* From different sample, not strictly comparable with analysis in column 1.

which are nevertheless more difficult to grind. The hardest of all is the flinty stone H, with an exceedingly fine grained porosity of 6.1% and a purity of only 77%. Pure calcite, as in the marble C, is apparently far more brittle than is its fine grained combination with siliceous impurities.

The remaining general relationship worthy of note is the consistent difference in properties and behaviour of the compact and shelly limes. This distinction is brought out clearly by the data presented in Table 6. For the purposes of this comparison the quite abnormal figures for the Chalk P have been omitted. The differences between the means for compact and shelly limes are significant for 10 out of 14 properties or values determined. The equally significant difference in aggregation has already been established. The shelly limes average 7.5% less carbonate than the compact limes. Far greater is the difference in porosity, the mean values for which are 10.7% and 32.1% for the compact and shelly limes respectively. This results in a correspondingly large difference in grindability, equivalent volume and equivalent calcite surface. The difference in irregularity is also most marked. The differences are all in favour of the shelly limes exposing a larger equivalent surface and in fact result in the shelly limes, as a group, possessing 50% greater equivalent calcite surface than do the corresponding fractions of the compact limes. It is interesting to compare the greater chemical reactivity revealed consistently by the coarser fractions of the shelly limes with the conclusions drawn by Hudson *et al.* (1937) from their observations on the reversion of superphosphate by different limes, referred to on page 136. It would now appear probable that the greater efficacy of the foraminiferal limestones in reverting superphosphate was due to their containing a higher percentage of superfine particles, a feature that has been shown to be characteristic of the pulverised compact limestones.

The beneficiation in carbonate content of the 20-40-mesh separates when they are sieved out and water washed is illuminating. In the case of the shelly limes, this separate gains on the average by 10.5% in purity, while the corresponding gain of the compact limes is only 2.6%, the difference proving highly significant. This is due to a difference in the way the impurities are held. In the compact limes the impurities are embedded in the fragments of limestone, hardly separable from them till further pulverising or solution release them. In the shelly limes, on the other hand, the impurities consist largely of sand, silt and clay that have lodged among the shell fragments and in their numerous interstices, and it is a measure of the very slight degree to which these limestones have been indurated, that a considerable portion of the siliceous impurities are still free to be removed by a stream of water. The truth of this was confirmed by an examination of two groups of compact and shelly limes, comparable in purity and porosity. The > 80-mesh portions of the compact limes when elutriated lost on the average 0.8% of fine sand and 1.2% of silt and clay, whereas similar fractions of the shelly limes lost 7.1% and 2.4% of these impurities respectively, yielding decidedly more sand, as would be expected. The result of this difference in the location of the impurities is that the ultimate carbonate particles derived from the shelly limes are considerably purer than the limestones themselves, and there is nothing

to suggest they differ appreciably in hardness or in solubility *per unit of surface* from the particles of the hardest crystalline limestones.

The magnesium content of the shelly limes is significantly greater than that of the compact limes, though the levels are low in either case. There is only a feeble correlation between magnesium content and percentage of non-calcareous impurities. The governing factor appears to be the shell origin, since the five crystalline compact limestones which are in fact highly altered shell limestones, are also relatively high in magnesium.

CONCLUSIONS

The results emphasise the great diversity of the South Island agricultural limestones, particularly in respect of their physical properties and the characteristically distinctive features of the different outcrops. The compact and the shelly limes reveal marked and consistent differences in their properties and behaviour on crushing. The differences in grindability are large and this, taken in conjunction with the fact that many of the harder stones require finer comminution to achieve the same equivalent calcite surface, must result in some considerable differences in the power consumed in the crushing process per ton of output, if products of equal availability are produced. The good correlation between grindability and the measured values for equivalent calcite surface lends some support to the widely held view that the more easily crushed stones need less reduction in particle size than do the harder stones, though this should not be used as an excuse for unduly coarse products. The fact that the equivalent calcite surface of the different limes, as measured by their chemical reactivity, can be predicted with some accuracy from their macroscopic physical characters is taken as evidence that the wide range in reactivity is due to differences in degree rather than of kind of external surface exposed. This is to be expected, since for all the differences in texture and hardness it is ultimately the calcite crystal that is involved, whether it be visible or microscopic, pure or intimately involved with siliceous impurities.

The considerable differences in carbonate content and in the equivalent surface of that carbonate, coupled with the equally wide differences in fineness, must result in great differences in the rate of supply of soluble calcium when the commercial limes are applied at the same rate per acre. It would seem possible, from the data reported here, that some limes could be several times more available, say, during the first year, than others. Yet liming recommendations are still made without any reference to the rapidity with which the calcium will become available. The implication of the results is that those limestones with a low apparent volume require a somewhat finer grinding in order to achieve the same equivalent calcite surface, but the application of this to the commercial crushed products has yet to be worked out.

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EFFECT OF SOIL ACIDITY ON GROWTH OF PASTURE PLANTS

II. A FIELD TRIAL WITH WHITE CLOVER (*Trifolium Repens*)

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Summary

Twenty white clover plants of different genotype were grown in plots of five soil treatments: lime, gypsum, untreated control, light sulphur, and heavy sulphur. The soil acidities produced ranged in pH from approximately 7.0 to 3.5.

The content of soluble salts in the acidulated soils was greater than would be expected from experience with soils of similar natural acidity.

The yields of the white clover plants were adversely affected by the two sulphur treatments, but other treatments did not cause significant differences.

There was no evidence of interaction between the different plants and the various soil treatments.

INTRODUCTION

It has long been recognised (Truog, 1918) that clovers and legumes as a whole grow poorly in acid soils. Jones and Levisohn (1951) showed that this is often due to nutritional causes by growing red clover (*Trifolium pratense*) successfully at pH 4 and pH 7 when sufficient compost was applied to supply essential nutrients. Donald (1941) reported Klapp (1938) as classifying certain of the commoner legumes in Germany on the basis of their frequency in soils of varying acidity. Of those listed, *Trifolium repens* was the only one prominent over the whole range of soils examined, being one of the most frequent on soils of each group from pH 3.4 to pH 8.5. Donald attributed this universality of white clover as "due in part to the great degree of polymorphism in the species".

Many plant species have strains or varieties that differ in their requirements for optimum growth and the acidity of the growing medium is one factor "often specific for different strains" (Lundegardh, 1931). Small (1951) lists numerous species which have varieties preferring different levels of soil acidity. Thus he reports Arrhenius (1926) as finding different oat varieties which showed maximum yields at each of the following acidity levels: pHs 4.9, 5.7, 8.4 and 9.0. Other workers such as Reid (1932) and Papadakis (1941) have reported similar results with various plant species.

In a previous trial (McNeur, 1953) it was found that when plants of two white clover strains were grown at five different levels of acidity, one strain gave approximately double the yield of the other at four acidity levels but at the fifth and most acid level both gave the same yield. These results, viewed in the light of the strain and varietal acidity preferences mentioned above, led to the suggestion that it might be worth developing a strain of white clover specifically for the

areas of very acid soil that occur in parts of New Zealand. The present trial was planned to investigate the position more critically and to examine the growth of different types of white clover in plots brought to different soil acidities, the levels varying in pH between approximately 7.0 and 3.5.

EXPERIMENTAL METHOD

Soil

The soil in the trial area is classed as Manawatu Silt Loam of Recent Origin and had been subject to normal station management for about twenty years.

Treatments

The following treatments were planned:—

Lime	pH 6.5 — 7.0 =	Treatment A
Gypsum (equivalent calcium to that in lime used)	pH 5.0 — 5.5 =	„ B
Untreated control	pH 5.0 — 5.5 =	„ C
Light sulphur	pH 4.0 — 4.5 =	„ D
Heavy sulphur	pH 3.0 — 3.5 =	„ E

After preliminary trials had been completed using soil in pots to determine the amounts of lime and sulphur required to produce the desired acidity changes, the following treatments were carried out on 22.9.48:—

Treatment A:	605 g. slated lime per sq. yd.
„ B:	1,406 g. gypsum „ „ „
„ C:	Untreated
„ D:	113 g. flowers of sulphur per sq. yd.
„ E:	582 g. „ „ „ „ „

Plot Layout and Planting

The layout was in the form of a “split-plot Latin square” with the soil treatments as the main plots and the different plants of white clover as the sub-plots. The main plots were 16ft. × 13ft. and the clover plants spaced 2 ft. 3 in. apart, the total area of land occupied by the trial being approximately one square chain.

Twenty white clover plants differing greatly in vigour, density and leaf size were selected for the experiment. As it was thought possible that plants with or without the enzyme linamarase and the glucoside lotaustralin (Corkill, 1940) might react differently to varying levels of soil acidity, plants differing in these characters were included. Fifty cuttings from each selected plant were placed in boxes of sterilised soil, and after establishment the 25 most uniform were chosen and were planted in randomised positions in each plot on 10.3.49.

Growth Records

Notes on plant growth were taken periodically, and after the plants became well established the herbage was cut and weighed. Green weights only were recorded as the evidence is that these are sufficient for comparisons within any species (Hudson *et al.*, 1933; Leonard and Clark, 1946). All plants were trimmed six months after planting and the first measurement cut took place on 29.11.49. Cutting and weighing were continued for twelve months from this date.

Acidity and Chemical Composition of Soils

The following determinations and analyses were conducted by Dr. W. M. H. Saunders and Mr. L. Blakemore of the Soil Bureau, Wellington:—pH; base exchange capacity; total exchangeable bases; sulphate soluble in water and soluble in ammonium acetate; and the water soluble cations calcium, magnesium, sodium, and potassium. These determinations were made on samples of 25 cores to 6 in. depth but were made on only one plot from each of three treatments—the control and the two sulphur treatments. In addition, so that the acidity changes could be followed after the treatments had been carried out, the pH of samples of the 0–3 in. and 3–6 in. layers were determined for all plots at various times.

Observational Trial

At one end of the experimental area an extra set of treated plots was prepared and on each of these rows of 7 pasture grasses and 8 pasture legumes were sown on 11.3.49. In addition to the main treatments, the following subtreatments were applied to all species: unfertilised; superphosphate at 3 cwt. per acre at sowing; and urea at 1 cwt. per acre six weeks after sowing. The treatments were not replicated and no measurements were taken, but notes on herbage growth and appearance were made periodically and all legumes were examined for nodulation.

RESULTS AND DISCUSSION

Rainfall

The rainfall at the Grasslands Division between the dates of soil testing is recorded in Table 1 so that this can be used in conjunction with the results of the determinations and analyses as recorded in later sections.

TABLE 1. RAINFALL BETWEEN DATES OF SOIL TESTING

Period	Rainfall	Progressive Total
	(in.)	(in.)
22.9.48 — 9.12.48	10.38	10.38
9.12.48 — 11.1.49	2.73	13.11
11.1.49 — 10.3.49	7.22	20.33
10.3.49 — 2.9.49	22.18	42.51
2.9.49 — 4.10.49	1.29	43.80
5.10.49 — 10.5.51	55.81	99.61

A proportion of this rainfall would be expected to percolate through the plot soils and to effect leaching, but it should be recorded that the plots in Treatment E (heavy sulphur) developed a fine structure that tended to seal the surface of the plot, and it is probable that this treatment received less leaching than the others.

Soil Acidity Changes

The trial area was sampled on 1.7.48 for preliminary acidification trials and for pH determination, and at this time the mean acidities recorded from random sampling were as follows:— 0-3 in., pH 5.6; 3-6 in., pH 5.4; 6-9 in., pH 5.5. The next determinations were made on 22.9.48 after individual plots had been marked out, and each plot was tested separately. In this test the samples used were composites of five cores of 0-6 in. and the acidities ranged from pH 5.0 to pH 5.4, the mean being pH 5.2 and the standard error per determination being ± 0.10 . For subsequent determinations, unless otherwise stated, the samples were also compounds of five cores per plot and the 0-3 in. and 3-6 in. layers were tested separately. Measurements of acidity on samples taken on 9.12.48 showed that the 0-3 in. layer had been changed more than the 3-6 in. layer, so the plots were dug to 6 in. and the spits of soil carefully inverted.

The effects of the treatments, which were carried out on 22.9.48, on the acidities of the plot soils is shown in Table 2.

TABLE 2. EFFECT OF TREATMENTS ON SOIL ACIDITIES AT DIFFERENT SAMPLING DATES
(mean and range of 5 replicates)

Treatments	Sampled 9.12.48 pH	Sampled 11.1.49 pH	Sampled 10.3.49 pH
A. Lime			
0 — 3 in.	6.8 (6.6 — 7.2)	6.7 (6.3 — 6.9)	6.9 (6.2 — 7.2)
3 — 6 in.	5.6 (5.4 — 6.0)	5.8 (5.5 — 6.3)	5.8 (5.1 — 6.1)
B. Gypsum			
0 — 3 in.	5.1 (5.0 — 5.3)	4.8 (4.6 — 5.0)	4.9 (4.8 — 5.1)
3 — 6 in.	4.8 (4.7 — 5.0)	4.7 (4.5 — 5.0)	4.7 (4.6 — 4.9)
C. Control			
0 — 3 in.	5.1 (5.1 — 5.2)	4.8 (4.7 — 4.9)	4.9 (4.9 — 5.0)
3 — 6 in.	5.2 (5.0 — 5.3)	4.9 (4.6 — 5.1)	5.0 (4.9 — 5.1)
D. Sulphur			
0 — 3 in.	4.0 (3.9 — 4.3)	3.9 (3.9 — 4.0)	4.1 (4.0 — 4.2)
3 — 6 in.	4.8 (4.7 — 4.9)	4.3 (4.0 — 4.8)	4.6 (4.4 — 4.8)
E. Sulphur			
0 — 3 in.	3.2 (2.9 — 3.4)	2.9 (2.8 — 3.1)	3.1 (2.9 — 3.4)
3 — 6 in.	4.1 (3.7 — 4.7)	3.6 (3.2 — 4.1)	3.7 (3.5 — 4.0)

The variation of the acidity of the untreated soil is of interest and is illustrated in Fig. 1 by the pH determinations made on soil from Plot 15 (Treatment C) at various sampling dates. From the uniformity trial of 22.9.48, it was found that the standard error per determination was ± 0.10 , so that differences between acidities recorded from September 1948 to July 1949 of ± 0.30 and from September 1949 to May 1951 of ± 0.06 , can be taken as significant at the 5% level. The variability shown is of particular significance when pH measurements are used by advisory services for assessing lime requirements. It is certain

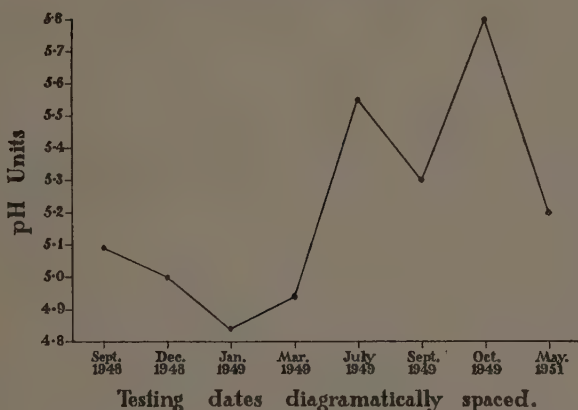


Fig. 1.—Line graph showing the acidity of the soil in Plot 15 (untreated control) at various times during the trial period.

that the recommendations for Plot 15 in the present trial would be very different if based on the samples taken in January or October, 1949.

This variation in soil acidity when measured at different times of the year has been well established by workers such as Gardner and Brown (1911), Swanback and Morgan (1930) and Hester and Shelton (1933). The extent of this variation seems to depend partially on the mean acidity, because Bayer (1926) found that while acid soils showed a continuous increase in acidity from May to September of 0.92 pH (northern hemisphere), alkaline soils showed no such regular change. Variations of similar magnitude were found by Kelly (1923) who noted changes of 1.0 pH during the year, with increase in acidity from July to October (northern hemisphere). These results agree with the findings in the present trial where the acidity increased from the late spring to the end of summer and early autumn, from which time the pH began to rise again to complete the cycle.

Table 1 shows that as a whole the various treatments have brought the soil acidities within the desired range, and final measurements made in May 1951 show that these have been maintained fairly well during the period of the trial.

Soil analyses

In Table 3 are presented results for pH, base exchange capacity, total exchangeable bases and percentage base saturation, as measured on the 0-6 in. layer from three representative plots at four sampling dates.

It can be seen that the sulphur treatments decreased the pH and the total exchangeable bases to a marked extent, and that these effects were maintained during the 2½ years between the initial treatment and the final analyses. A more complete picture can be obtained by examining further results at 4.10.49 when detailed analyses were carried out. These additional results are shown in Table 4,

TABLE 3. CHEMICAL ANALYSES OF SELECTED PLOTS

Sampling date		pH	B.E.C.	T.E.B.	% B.S.
Treatment C					
22.9.48	} untreated	5.3	14.6	9.9	66
2.9.49		5.3	15.4	9.8	62
4.10.49		5.8	15.8	9.9	63
10.5.51		5.2	14.3	9.5	66
Treatment D					
22.9.48	Before treatment	5.5	14.6	10.1	68
2.9.49	} After "	4.8	14.5	6.5	43
4.10.49		5.0	15.1	7.4	49
10.5.51		4.5	14.3	5.9	41
Treatment E					
22.9.48	Before treatment	5.4	15.2	9.4	60
2.9.49	} After "	3.5	14.5	2.4	15
4.10.49		3.7	15.4	2.6	17
10.5.51		3.7	14.5	2.3	16

TABLE 4. SOIL ANALYSES 13 MONTHS AFTER SULPHUR TREATMENTS
(expressed as m.e.%)

Treatment	pH	T.E.B.	Exchangeable cations			SO ₄		Water Sol. Cations			
			Ca.	Mg.	K.	Sol. in water	Sol. in NH ₄ OAc	Ca.	Mg.	Na.	K.
C	5.8	9.9	8.8	1.1	0.4	0.9	1.2	0.3	tr.	0.4	tr.
D	5.0	7.4	6.4	0.9	0.35	1.5	1.8	0.6	tr.	0.4	tr.
E	3.7	2.6	1.7	0.5	0.3	4.4	4.3	3.9	tr.	0.5	tr.

These figures show the effect of the sulphur treatments in decreasing the total exchangeable bases, the element most affected being calcium, then magnesium, while potash was hardly altered. At the same time there was a marked increase in the water-soluble sulphate and water-soluble calcium, indicating that the sulphur after acidification had converted a proportion of soil calcium to calcium sulphate. Some of this had been removed from the soil by leaching but, particularly in the case of Treatment E, it is clear that the amount of rain penetrating the plots had not been sufficient to ensure complete removal of calcium sulphate. Thus, at the time of this test, although the acidity had been increased, there still remained a greater proportion of soluble salts in the acidified soil than would be found in a natural soil of similar pH.

From this evidence it would appear that care should be taken in applying results obtained from plant growth on artificially acidified

soils unless these have been very thoroughly leached. The chemical changes due to artificial acidification are being further investigated.

Plant yields

The analysis of variance of plant yields is given in Table 5. For this analysis the most acid treatment (E) was completely omitted. Plants in these plots survived for a short time, probably on account of the potting soil on their roots at transplanting, but all were dead long before the end of the trial.

TABLE 5. ANALYSIS OF VARIANCE OF TREATMENT YIELDS

Source	Sums of Squares	d.f.	Mean Sq.	F	F required 5% (1%)	Result
Rows and columns	8,266.45	8	1,033.31	3.99	3.44 (6.03)	*
Treatments	4,171.38	3	1,390.46	5.37	4.07 (7.59)	*
Error (1)	2,072.67	8	259.084			
Plants	62,422.00	19	3,285.37	34.40	1.61 (1.94)	***
Plants $\times$ treatments	3,621.62	57	63.54	—	1.40 (1.60)	—
Error (2)	29,034.88	304	95.51			
Total	109,589.00	399				

* Significant at 5% level

*** Significant at 0.1% level

The treatment means for production per plant were : A, 21.63 oz.; B, 24.1 oz.; C, 23.95 oz.; D, 16.12 oz.; E, nil. The difference between pairs of these for significance at 5% level is 5.25 oz. Treatment D caused a significant lowering of yield when compared with Treatments A, B or C, which did not differ significantly. From these results it can be concluded that the untreated control soil (C) contains sufficient calcium and sulphur for white clover growth, and that the pH of the control soil is suitable for growth of white clover. The pH of the untreated soil must be fairly near the lower limit for maximum white clover growth because the lowering to the level found in Treatment D resulted in significant yield decrease. There is some evidence from the observation trial (see later) that this reduced growth at the lower pH level may be due to a reduction of available phosphate as a result of the increase in acidity, but this is not proved.

The effects of the soil treatments on white clover growth are in general agreement with those of a trial previously reported (McNeur, 1953), where the optimum acidity for growth as estimated from response curves was pH 5.5 and 5.3 respectively for two different white clover plants. In the present trial, however, the mean plant yield did not decrease with decrease in acidity as it did in the former trial.

When the soil treatments are disregarded it is found there are wide differences between the herbage yield of different plants. The mean yield per plant for the total measurement period ranged from 47.6 oz. to 5.1 oz. but there was no evidence of interaction between plants and soil treatments. This trial was designed primarily to see whether there

was any variation in the preferred acidity of single plants of white clover, and this lack of interaction indicates that no particular plant of the white clovers used preferred or tolerated acidity levels different from those generally preferred or tolerated. Thus, there is no evidence from this trial that a special strain of white clover should be developed for use on the more acid soils.

Observational trial

For the comparison of the effects of the soil treatments on the sown rows of the different species, the results four months after sowing will be considered, as by this time seedlings were well established and distinct differences could be seen. The acidities of these plots at this time were as follows: A, pH 7.6; B, pH 5.1; C, pH 5.6; D, pH 4.0; E, pH 3.3.

(a) *Grasses*: In the most acid Treatment E, the only plants to become established were of *Agrostis* species and *Holcus lanatus*, and the growth of these appeared normal in all respects. In all the other plots the majority of the grasses gave good growth, but a few, such as *Cynosurus cristatus*, showed reduced herbage production in Treatment D. The reduction was completely overcome by the use of either phosphate or nitrogenous fertilisers. The species *Festuca rubra* var. *commutata* and *Agrostis tenuis*, which are of importance on playing greens, were of interest in that they grew outstandingly well on Treatment D.

(b) *Legumes*: The legumes used included species of *Lotus* and *Trifolium*, and none of these became established on the extremely acid soil of Treatment E. On the less acid soil of Treatment D all but one of the species germinated and established well, and even though the growth was poorer than that on the less acid soils this was usually improved where phosphate or nitrogen was applied. *Trifolium repens* was one of those species that had the growth visibly reduced on this plot but where phosphate or nitrogen had been used the growth was as good as that on the less acid plots. All species grew well on each of the Treatments A, B and C and most showed improved growth with the addition of superphosphate. *Trifolium pratense* was different from all other species used, in that its growth was better on the limed plot than on any other, it was slightly reduced on Treatments B and C, while on Treatment D its growth was very poor indeed, and neither fertiliser caused any improvement. This result is in line with that from the earlier trial previously mentioned, where the same variety of red clover (Montgomery) gave progressively reduced growth when the acidity was increased below pH 6.0.

CONCLUSION

(1) Although the white clover plants tested in this trial varied widely in both genotype and phenotype, there was no evidence of any of them reacting differently from the others to the various levels of soil acidity used, so that there appears to be little point in producing a special strain of white clover for the more acid soils of New Zealand.

(2) The powdered sulphur caused the desired increases in soil acidity but there were still present soluble calcium salts even in the most acid soil a year after treatment. The artificially acidified soils were therefore not comparable to naturally acidified ones, at least until considerable leaching had taken place.

(3) There were periodical marked changes in the measured acidity of the untreated soil, confirming the fact that a pH measurement at any one time of the year cannot be regarded as absolute.

(4) The soil in Treatment E was too acid for white clover growth and no plants gave any production. However, certain grasses, *Agrostis* species and *Holcus lanatus*, did establish from seed and grew successfully on this soil.

(5) Treatment D increased the acidity to cause a reduction in white clover yields, when compared with the control, but there was some evidence that this could have been counteracted by an application of superphosphate.

(6) The other three soil treatments produced equal yields of white clover, the extra calcium or reduced acidity causing no growth increase over the control soil despite the fact that the control soil was strongly acid.

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EFFECT ON HONEY BEES OF DDT PLUS SUPERPHOSPHATE APPLIED AS A DUST TO WHITE CLOVER PASTURE

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Summary

DDT plus superphosphate was dusted over 12 acres of white clover pasture at the rate of 2 lb. of 100% p.p.i. DDT per acre. This mixture was applied in the manner recommended for grass grub control.

It was established by marking and counting, that bees from a nearby experimental apiary were collecting nectar extensively from the dusted area.

Very definite evidence was obtained that the DDT repelled bees for some days after application. Field bees collected from the dusted clover flowers did not show a high mortality and no adverse effects on the hives were observed.

It is concluded that such dusting would cause only negligible losses of bees in neighbouring apiaries.

INTRODUCTION

Until recently the grass grub (*Costelytra zealandica* (White)) and the subterranean grass caterpillar (*Oxyacan* spp.) caused great damage to pastures in New Zealand, resulting in much economic loss. Then Kelsey^{1, 2} showed that these insects could be controlled by the application of DDT or benzene hexachloride. These control measures have proved so successful that they are now being applied extensively in New Zealand.

The large scale use of DDT and benzene hexachloride, both of which are stomach and contact poisons to honeybees, has naturally been closely watched by commercial beekeepers, the Horticulture Division of the New Zealand Department of Agriculture and the Wallaceville Animal Research station.

Investigations carried out overseas would indicate that DDT does not constitute a serious danger to bees when dusted on cotton plants³ or alfalfa^{4, 5}. On the latter plant⁵ and on dandelion flowers⁶ it has been shown to have a repellent effect on the bees. Kelsey^{1, 7}, warns against the application of these insecticides to pastures when they may be attractive to honey bees. It is recommended that to secure maximum benefit from the fertilizers with which the insecticides are generally mixed application should be made about August to November⁷ or September to November¹. In some parts of New Zealand the use of these insecticides in November, or even October, might coincide with the spring activity of honeybees, and great care would be necessary to avoid application to plants which bees were working. Farmers have not always been able to apply insecticides during the recommended period and a few cases were reported in Canterbury of their application

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in the summer months, and of bees collecting nectar from the treated pastures. Losses of field bees through this practice were claimed to have taken place but could not be substantiated. Strong winds, particularly from the North West, are prevalent in Canterbury, and often cause heavy losses of field bees. If such losses came at a time when an insecticide had been applied, a beekeeper might incline to blame the new factor. However, in view of the lack of definite knowledge the Entomological Research Station and field officers of the Department of Agriculture have urged farmers to take every care when applying insecticides.

The white-clover pasture which grass grub and subterranean caterpillar infest supplies the bulk of the honey crop in most parts of New Zealand. If an insecticide were applied when bees were visiting it in large numbers because of a honey flow they would be exposed to the maximum danger. In this experiment DDT was applied to a clover pasture at such a time. The usual method of applying the DDT on farms is in the normal superphosphate topdressing, or with up to 2 cwt. of lime per acre. In the experiment, superphosphate was used and the DDT applied at the maximum rate of 2 lb. of 100% p.p.i. DDT per acre.

DDT is much more widely used than benzene hexachloride for grass grub and subterranean caterpillar control because it is cheaper, its insecticidal power persists longer, and it is more pleasant to handle. Accordingly, it was used in the experiment, although benzene hexachloride is much more toxic to honey bees. It was hoped that the conclusions drawn from the experiment would be of value in deciding what precautions were necessary for the safe use of DDT.

DATA RELATING TO EXPERIMENTAL AREA

Location of Experiment

The two experimental areas used were situated near Lyndhurst, approximately 17 miles in a straight line from Ashburton in Canterbury (See Fig. 1.). Grass grub and subterranean caterpillar infestation was heavy in the country surrounding Ashburton until it was brought under control by treatment, mainly with DDT. This district is an excellent one for beekeepers, and heavy crops of honey are produced from the clover pastures. It thus provided an ideal site for the experiment.

Originally two apiaries had been set up in an area south-east of Ashburton which was free from commercial apiaries. However, due to the light soil here drying out unexpectedly the clover ceased to yield nectar, and these sites had to be abandoned. The hives in one apiary were too heavy with honey to move but those in the other were transported to the Lyndhurst site and used to provide bees for the area to which DDT plus superphosphate was applied (See Fig. 2). No hives were available to provide bees for the control area to which superphosphate only was applied. However, there are many commercial apiaries in the Lyndhurst district and it was considered these would ensure an adequate number of bees.

Areas Treated with DDT plus Superphosphate

The 12 ac. area (264×220 yd.) and a 1 ac. area (147×33 yd.) both of which were treated with DDT plus superphosphate, were

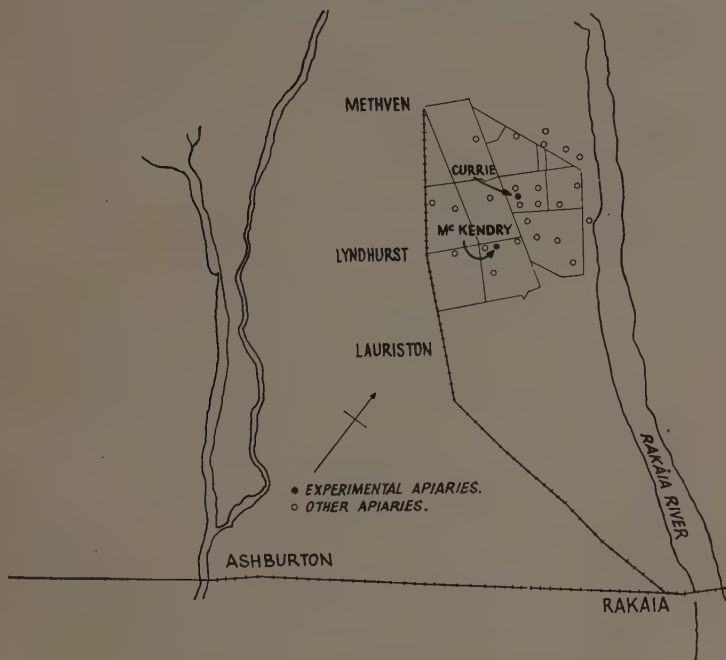


Fig. 1.—Map of experimental site.

marked out in a field of white clover pasture (*Trifolium repens*). The pasture was thick with clover flowers, evenly distributed, and in a condition of maximum attractiveness to bees. The clover was interspersed with a light growth of rye-grass (*Lolium perenne*), but there was no red clover and other floral species were almost completely absent. The growth of clover was not rank but close to the ground. The apiary of 12 hives was placed immediately behind a 12 ft. high hedge which provided shelter. The bees crossed this easily, and flight lanes of bees working the field were soon well established (See Fig. 2).

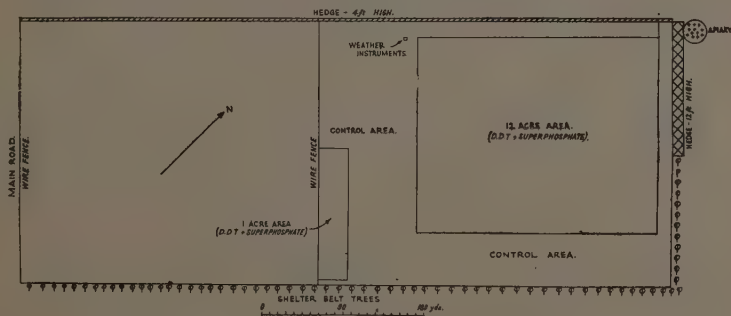


Fig. 2.—Plan of area treated with DDT plus superphosphate.

Control Area Treated with Superphosphate Only

This area, distant one mile from the other, was also of 12 ac. (264×220 yd.) and the clover pasture was in similar condition. Unlike the other areas, however, it was closely surrounded by ploughed fields and pasture unattractive to bees. It was also more sheltered from the prevailing wind. Nearby commercial apiaries supplied ample bee coverage (See Figs. 1 and 3).

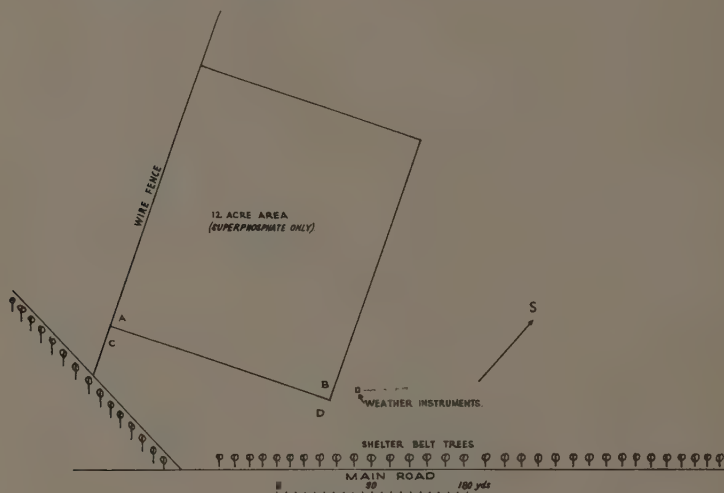


Fig. 3.—Plan of area treated with superphosphate.

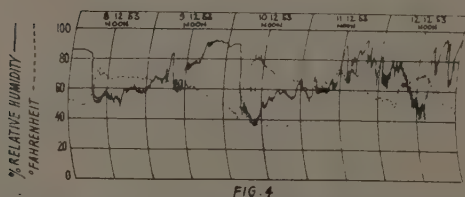


FIG 4

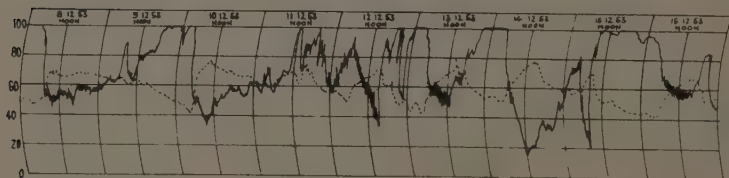


FIG 5

Fig. 4.—Thermo-hygrograph readings at area where superphosphate only was applied.

Fig. 5.—Thermo-hygrograph readings at area where DDT plus superphosphate was applied.

TABLE 1. WEATHER CONDITIONS AND GENERAL INFORMATION

Date	Rainfall during 24hr. ending 10 a.m. (in.)		Weather	Bee Activity	General
	Control Field (Super- phosphate only)	Treated Field			
1953					
Dec. 5	—	—	N. W. gale, sunny.	Little bee flight except in sheltered positions.	
6	0.06	0.07	Slight N.E. breeze, light rain mornings, becoming heavier in afternoon.	No bees flying.	
7	1.52	1.69	Calm, light rain.	No bees flying.	
8	0.09	0.13	Strong N.W. wind, no rain, sun early in morning then becoming overcast.	Clover flowers unattractive to bees even in sheltered positions.	Pasture still wet in morning.
9	—	—	Strong S.W. wind, less wind in afternoon, overcast.	Bees active in more sheltered field.	
10	—	—	Strong N.W. wind, sunny morning, overcast afternoon.	Honey flow.	
11	—	—	Almost calm, shower threatens at 11 a.m., overcast, showers from noon to 3 p.m. then calm and sunny.	Honey flow.	DDT plus superphosphate mixture applied by 8 a.m. and superphosphate by 9 a.m.
12	0.04	0.06	Very slight S. breeze, hot sun alternating with overcast sky.	Honey flow.	Weather ideal for honey flow; Patches of clover commencing to seed.
13	—	—	Calm, sunny in morning, cloudy in afternoon, cool N.E. breeze.	A heavy honey flow.	
14	—	—	Slight N.E. breeze morning, sunny, strong N.W. wind afternoon.	In afternoon bees not working clover even in warm, sheltered positions.	DDT plus superphosphate mixture applied by hand to one acre by 11.30 a.m.
15	—	—	Strong S. wind, overcast, rain commenced 11 a.m.	No bees flying.	
16	—	1.11	Slight N.E. breeze, sunny.	A heavy honey flow.	
17	—	—	Strong N.W. wind, overcast.	No honey flow even in warm sheltered positions.	

Weather Observations

Thermo-hygrographs and rain gauges were installed at both experimental areas. Wind and other conditions were also noted (See Figs. 4 and 5, and Table 1).

Application of DDT plus Superphosphate, and Superphosphate Alone

Four pounds of 50% p.p.i. DDT was thoroughly mixed by hand with each cwt. of superphosphate and the mixture applied in this strength to each of the 12 ac., i.e. 2 lb. of 100% p.p.i. DDT per acre.

The purity of the DDT and the efficiency of the mixing were checked by the Entomological Research Station, Ashburton. The superphosphate used was a very finely ground and dry sample of a well-known commercial brand containing 44-46% of calcium acid phosphate.

The DDT plus superphosphate and the superphosphate were both applied to the experimental areas by Munro gravity-feed topdressers which had a 2 ft. 6 in. drop and which gave an even spread of fertilizer with no separation.

It was essential that topdressing should be done in a dead calm to prevent drifting of insecticide and superphosphate outside the experimental areas. Rain was also to be avoided as it would wash the insecticide off the clover blossoms. It was equally important that topdressing should be carried out at a time when the clover was secreting nectar, and bees were collecting it in large numbers, so that an appreciable number could come in contact with the insecticide. Finally, if these exacting conditions could not be satisfied in a fairly short period, the clover was likely to go to seed and lose its attractiveness to bees. Table 1 shows that owing to unsettled weather it was not possible to meet these requirements until 11th December, when all conditions were ideal early in the morning and topdressing was carried out.

Application of DDT plus superphosphate was finished by 8 a.m. The weather was calm at first but later there was a breeze of about 12 m.p.h. The temperature at the time of application was 63°F., and the relative humidity 55%. No bees were present at the time of application but they commenced to visit the area at 8 a.m.

The superphosphate was also applied on 11th December, the operation being finished by 9 a.m. The temperature during application was 70°F., relative humidity 60%, and a calm prevailed. Equipment similar to that employed for topdressing with DDT plus superphosphate was used. Weather conditions were ideal for application of the superphosphate. No bees were present during the application but they commenced visiting the area shortly afterwards.

The men applying both topdressings were very experienced, and the dusts were distributed evenly, without any drifting outside the marked areas. The operations were carried out under the supervision of an officer of the local Entomological Research Station.

At noon on the day of dusting, light rain commenced and continued until 3 p.m. when the weather cleared and became hot, sunny, and completely calm. Six points of rain fell on the area topdressed with DDT plus superphosphate, and 4 points on the other area. The rain did not

appear to wash off much of the dusts which were now sufficiently wet to stick to the pasture. The strong winds usually prevalent in this district would probably have quickly blown off much of the dry dust. No further rain fell until the 15th December when heavy rain commenced and continued until the 16th by which time 1.11 in. had fallen. Even after this heavy fall the topdressing could still be seen on the pasture in the two areas.

An area of 1 ac. was dusted by hand with DDT plus superphosphate of the same composition as used for the 12 ac. area. Application was finished by 11.30 a.m. on 14th December under calm and sunny conditions. A strong North West wind prevented bees flying in the afternoon, and heavy rain commenced the following day and continued until 1.11 in. had fallen. This area was accordingly used mainly for the collection of clover flowers for DDT estimations.

EXPERIMENTAL PROCEDURE

The following methods were used to assess the effect of the DDT plus superphosphate on the bees in the experimental hives:

(i) *Counts of Field Bees*

Counts of field bees were made in the areas treated with superphosphate, DDT plus superphosphate, and an area designated "control area" in Fig 2. The pasture in the "control area" was the same as in the 12 ac. area treated with DDT plus superphosphate. Counts from these two areas were expected, when compared, to show if the DDT plus superphosphate had any repellent action on the bees.

The method of counting was based on that described by Linsley⁵. Two operators walked down the long axes of the 12-ac. areas and the control area making complete sweeps at ground level with landing nets of 14 in. diameter. Each operator made 200 sweeps in one direction and then 200 in the reverse direction. The bees trapped by this method were counted, and the total number of bees caught by the two operators (800 sweeps) were plotted to give the graphs shown in Figs. 6 and 7. The same two operators worked together throughout the experiment. This method was found to give a most reliable and consistent picture of the density of bees on the pasture.

Superphosphate Area: This area was more sheltered than the one to which DDT plus superphosphate was applied. Consequently, it was not much affected by the strong North West winds which reduced bee flight over the other area on the 8th and 9th December. Bee counts in the superphosphate area were high on the 8th, and highest of all on the 9th, when there was a honey flow. A smaller honey flow occurred on the 10th. The superphosphate was applied by 9 a.m. on the 11th. At noon after the application 48 bees were collected and 25 bees in the afternoon (See Fig. 6). On the 12th there was a honey flow. Unlike the DDT plus superphosphate area this area was not surrounded with clover pasture suitable for control counts of bees. However, just outside the length of marked area AB was a strip CD of clover pasture of similar composition (See Fig. 3). Sweeps along these two strips at noon on the 12th showed no significant difference in density of bees. No observations were made after the 12th. It was not considered that bee counts were reduced by the application of the superphosphate.

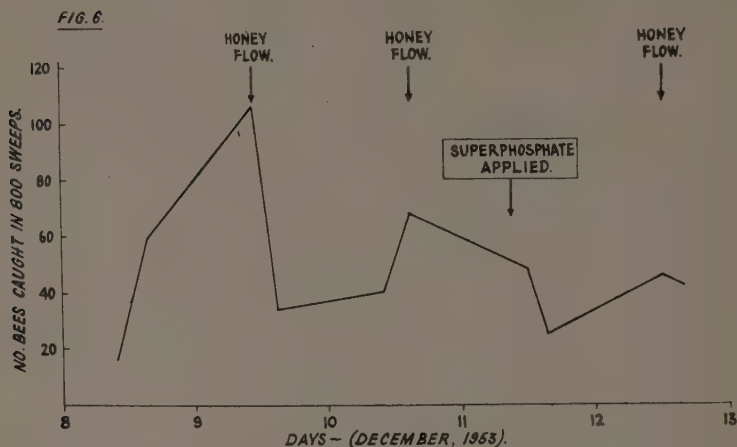


Fig. 6.—Bee-counts on area treated with superphosphate.

Repellency of DDT: The DDT plus superphosphate was markedly repellent to bees on the day it was applied. On the morning of application weather conditions were ideal, and there was a heavy honey flow. But, although the untreated control areas were being heavily worked by bees, these were reluctant to settle on clover flowers in the treated area, and many appeared to be hovering in the air a short distance above pasture level. In spite of the light rain which fell between noon and 3 p.m., repellency was still apparent when bee activity resumed. Bees were frequently seen to alight on stalks of clover flowers, clean themselves, and take off without attempting to collect nectar. None of these effects was noticed in the area treated with superphosphate which appeared completely lacking in repellency. The same repellency was noticed immediately after application in the area of one acre treated with DDT plus superphosphate. No visual evidence of repellency was apparent on the day following the application of the fertilizer.

Very definite evidence of repellency was furnished by the bee counts in the area treated with DDT plus superphosphate and the control

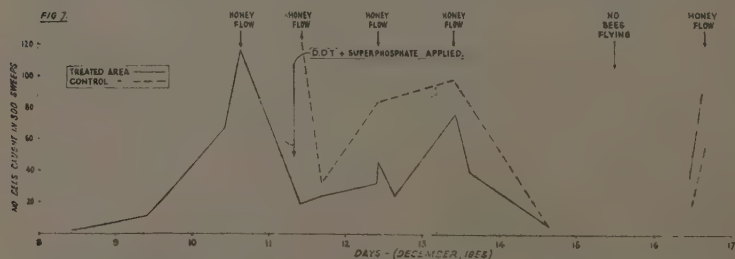


Fig. 7. —Bee-counts on area treated with DDT plus superphosphate and on control area.

areas. (See Fig. 7). Bee counts were low on the 8th and 9th December because of adverse weather. On the 10th, the weather improved, there was a honey flow, and counts were high. The DDT plus superphosphate was applied by 8 a.m. on the 11th. During the morning, weather conditions were ideal and there was a heavy honey flow. But, although 122 bees were collected in the untreated control area, only 19 were collected in the treated area. Light rain commenced at noon but cleared at 3 p.m. when bee activity resumed, although the honey flow was now greatly reduced. Bee counts in the afternoon were 24 on the treated area and 32 on the control area. At the time the sweeps were made on the control area the weather suddenly became cool and overcast, reducing bee activity, and depressing the bee count which would have been much higher if it had been made a few minutes earlier. On the 12th and 13th there were honey flows, and again bee counts were much higher on the control area than the treated one. On the afternoon of the 14th, bees were not collecting nectar from clover even in sheltered positions, and on the 15th there was no bee flight owing to heavy rain. There was again a honey flow on the 16th when counts for the first time were higher on the treated area than the control. The bee counts show that the DDT was repellent to bees from the time of application on the 11th until the 14th. The repellency is attributed entirely to the DDT as no evidence was obtained that the superphosphate exerted this action.

(ii) *Marking of Bees*

The evidence obtained from bee counts shows that the clover pasture was being heavily worked by bees both before and after dusting with DDT. However, as commercial apiaries were within bee range, it was also necessary to discover what proportion of these bees came from the 12 experimental hives.

This was done by marking bees as they left the hive with aluminium paint powder applied by a device developed by Nairn⁹.

Markers were put on all twelve hives at 2 p.m. on the 12th December and removed at 3 p.m. on the 13th. On the 13th, bees collected in sweeps were anaesthetised by placing the landing nets in containers and filling these with CO₂ from portable cylinders. Marked bees could readily be distinguished. This method showed that at least 75% of the bees collected on the 13th came from the experimental apiary. On the 16th the percentage of marked bees was 90%.

Since the start of the experiment the direction of flight lanes had shown that bees from the experimental hives were heavily working the area.

It was thus established that field bees in the area to which DDT was applied came mainly from the experimental hives.

(iii) *Mortality in Field Bees*

The most satisfactory method of studying the toxic action of the DDT dust was considered to be by the caging and observation of field bees.

Field bees were picked off clover flowers in the 12-acre treated area and placed in cages which were kept in an incubator room at 80°F. The cages were supplied with feeders containing sugar syrup. Control

bees collected from untreated areas showed a mortality of only 1% in 96 hr.

Because of the repellent action of the DDT it was often difficult to collect sufficient bees, particularly during the first day after dusting.

It will be seen from Table 2a that mortality, for each of the three lots of bees collected within a period of a day from the time of dusting, was 14% within 24hr. of caging. The toxicity of the DDT did not appear to be affected appreciably by the very slight rain (6 points) which fell on the day of dusting, but the heavy rain (111 points) on the 15th December reduced toxicity.

TABLE 2. MORTALITY IN CAGED BEES COLLECTED FROM FIELD TREATED WITH DDT PLUS SUPERPHOSPHATE

(a) At 8 a.m. on 11th December, 1953 and (b) At 11.30 a.m. on 14th December, 1953

No. Bees Collected	Time and Date of Collection.		Bees Dead After :					
			24 Hr.		48 Hr.		96 Hr.	
			(No.)	(%)	(No.)	(%)	(No.)	(%)
(a) 21	10-11 a.m.	11/12	(3)	14	(4)	19	(8)	38
14	5 p.m.	11/12	(2)	14	(2)	14	(4)	29
22	10 a.m.	12/12	(3)	14	(4)	18	(6)	27
21	11 a.m.	13/12	(2)	9.5	(5)	24	(7)	33
11	8.30 p.m.	16/12	(1)	9	(1)	9	(1)	9
(b) 13	11 a.m.	16/12	(0)	0	(2)	15	(4)	30
15	3.30 p.m.	17/12	(0)	0	(0)	0	(0)	0

Table 2b shows results of cage tests on bees collected from the one acre area dusted on the 14th with DDT. Bee activity was low at the time of application and this coupled with the repellency of the DDT rendered it impossible to collect any field bees on the day it was applied. Heavy rain commenced the following day and by the 16th, 111 points had fallen. Bees collected on this and the succeeding day showed no mortality within 24 hr., proving that the rain had washed off most of the DDT.

Results show a low toxicity for the DDT. No dead or affected bees were noticed on the treated area, and bees and other insects collected in landing nets appeared normal.

(iv) *Observations at the Hive*

The hives were examined at intervals during the experiment and a month later. At all times hive activity was normal, and no bees affected with DDT poisoning were observed.

The ground was cleared in front of each hive and counts of dead bees brought out were made daily. These averaged a total of 250 bees

daily for the six days before dusting, and 165 daily for the six days after dusting. These figures are not reliable because maggots were observed picking up the dead bees. The mortality observed was no doubt largely due to the strong North West winds which frayed the bees' wings.

During the period 4th to 14th December, the hives collected an average of 40 lb. of honey each. Later, they collected so much honey that even the brood chambers were partially filled.

Analytical Procedure

(i) *Sampling*: The hazard to which bees will be exposed in practice is primarily due to the insecticide held in the flower heads. For this reason the following method of sampling was used to derive the quantity of DDT per flower. Two hundred clover flowers were picked at random along a line parallel to the long axis of each trial area, the collections made prior to top-dressing being used as controls. The flowers were counted into 1 lb. amber honey jars with screw-cap lids and stored as soon as possible in a cold room at 5°C. till analysed a fortnight later. Daily samples were taken from 9th to 17th December, when the main experiment concluded. One further sample was taken on 8th January from the 12-acre plot.

(ii) *Extraction Procedure*: 200 ml. of redistilled carbon tetrachloride was added directly to each collection jar. This was alternately shaken and stood at frequent intervals for one half hour. The contents were then poured into a large filter funnel, containing a cotton-wool plug in the stem, and collected in a 200-ml. flask. The extract was dehydrated by adding 15 g. of anhydrous sodium sulphate and shaking till the carbon tetrachloride was clear. All extracts were securely stoppered and stored at 5°C. till analysed.

(iii) *Removal of Interfering Pigments*: Pigments and extractable materials that may have given extraneous colours in the final stages of colour development were successfully removed with activated alumina as described by Norton and Schmalzreidt¹⁰. In preliminary tests, 4 g. of alumina (in a 13 mm. diameter column) was quite sufficient to remove interfering substances from 25-ml. aliquots of the carbon tetrachloride extracts—the largest aliquots used in the series. In addition, the alumina was tested for possible catalytic breakdown of DDT in the following way:

Four 25-ml. aliquots of the untreated-clover control extract were pipetted off and to three of these, 10 µg. of pure p.p.i. DDT added. These four solutions were passed through four prepared alumina columns. Each column was washed three times with 10 ml. portions of carbon tetrachloride and DDT determined in the eluates as described under "Estimation".

The untreated clover control blank showed negligible absorption at 600 mµ. Recovery of added DDT averaged 97% at the 10 µg. level. This showed that DDT was not decomposed by the alumina treatment and established the quantitative basis of the procedure.

(iv) *Estimation*: The Schechter-Haller¹¹ colorimetric method was used following nitration with oleic acid as recommended by Clifford¹². Other modifications are given in a brief outline of the method.

The carbon tetrachloride eluate from the alumina column is collected in a 175-ml. flat-bottom flask fitted with a B24 ground glass joint. All except 5-10 ml. of solvent is recovered by distillation and the residue transferred to an 8 in. $\times$ 1 in. test-tube with a B24 joint. Two 5-ml. carbon tetrachloride washings of the flask are added to the test-tube followed by 10 mg. of oleic acid and three glass beads. The solvent is then completely removed from the tube with the aid of suction on a boiling water-bath.

The residue is nitrated as described by Wichmann *et al.*¹³ using 5-ml. of nitration mixture.

When nitration is completed, the tube is cooled, 15-ml. of ice-cold distilled water added and mixed by swirling, and the tube placed in an ice-cold water-bath. 15-ml. of benzene are accurately measured into the tube which is securely stoppered and shaken vigorously for two minutes. When the phases have separated, the lower acid layer is removed by suction through a fine capillary tube¹⁴ which is passed down through the upper benzene layer. The benzene is now shaken for 1 minute with 10-ml. of ice-cold 10% potassium hydroxide and the latter withdrawn through the capillary tube as described above. This step is repeated until no further yellow colour develops in the alkali (usually 4-6 washes).

The final potassium hydroxide wash is completely removed, 2 g. of anhydrous sodium sulphate added, and the tube thoroughly shaken for a further two minutes. When the benzol has regained room temperature, suitable aliquots are transferred to a 50-ml. Erlenmeyer flask, gently evaporated to dryness on a water-bath, then heated in an air oven for one hour at 100°C¹².

The dried residue can now be dissolved in benzene and the sodium methylate reagent added. The blue colour of the p.p.i. DDT nitration product is compared with standards in a spectrophotometer at 600 m μ . Where the DDT content of the original sample was unknown, it was found convenient to take 1-ml. aliquots of the benzene and mix directly with 2-ml. of sodium methylate for visual comparison with a standard to determine the approximate DDT level. Suitable aliquots for the final reading can then be taken from the remaining benzene without having to repeat the whole estimation. The method when rigidly followed is highly reproducible and accurate.

Results of Analyses

Each point on Fig. 8 represents the average amount of insecticide on each of the 200 flowers of one collection. For the 1-ac. plot, these points lie on a smooth curve. In the 12-ac. area, however, considerable variation of the DDT level from day to day is evident.

The level of DDT per flower is 15-18 μ g. on the day of application. It is seen that this level rapidly dropped 70% in two days in the 1-ac. field and the same amount in 5 days on the larger area. The actual levels in both places were then the same at 4.8 μ g. per flower, despite the fact that the topdressing in the 1-ac. field was applied three days after the other.

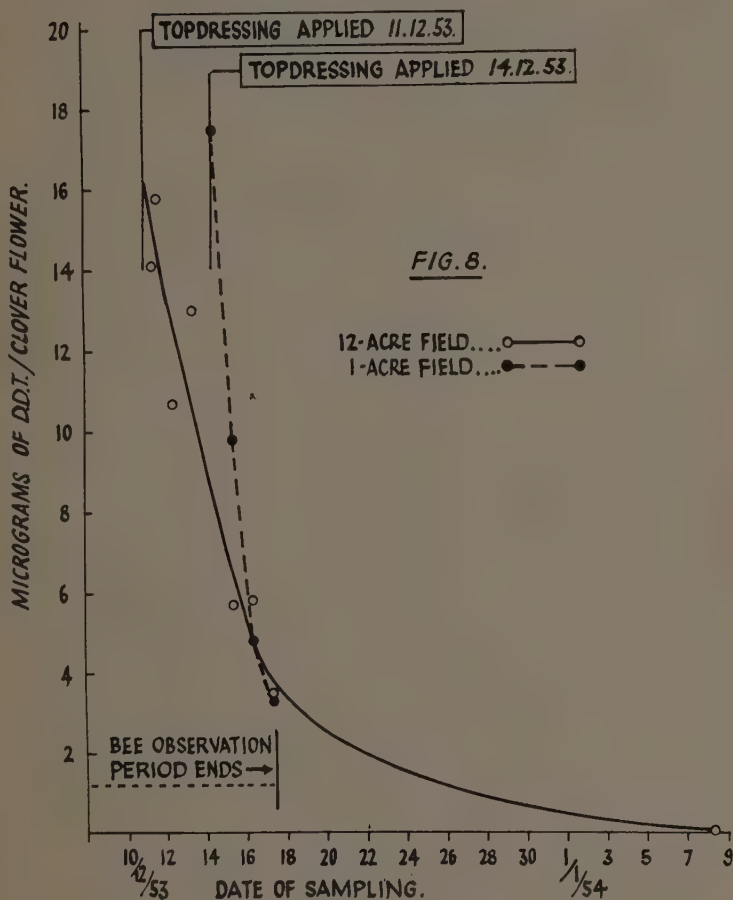


Fig. 8.—Persistence of DDT residues.

This rapid loss in the small field is undoubtedly due to the strong winds and the heavy fall of rain on the 15th December. Conditions in the 12-ac. field were calm and dry for 4 days after topdressing and the 6 points of rain which fell on the 11th December, had little effect on the DDT as shown by the bee mortality counts in Table 2.

It is reasonable to conclude that by the 17th December, the DDT remaining was firmly lodged on the flowers, and its disappearance from this date would be a gradual process. This would justify the continuation of the curve as shown to accommodate the last sample taken on the 8th January

This logarithmic pattern of insecticide loss in the field is a general characteristic of most insecticides and has been noted in previous trials at Wallaceville.

As the results are not expressed on a dry-matter basis but on actual DDT per flower, this depletion of DDT is due almost entirely to weathering and to a smaller extent to the daily opening of new flowers. The latter would contain little or no DDT but would obviously be included in the random sampling. Observations showed that to reach maturity 6 days were required for clover flowers just commencing to show white florets.

DISCUSSION

The results of this experiment in which DDT plus superphosphate was applied at the rate of 2 lb. of 100% p.p.i. DDT per acre to a clover pasture thick with flowers of maximum attractiveness to bees would indicate:

(i) That DDT plus superphosphate is strongly repellent to bees. The repellency is due to the DDT as superphosphate alone has no repellent effect.

(ii) Although mortality of bees does take place on dusted pasture, repellency is so strong that only negligible losses would occur in neighbouring apiaries. However, the precautions at present recommended should not be relaxed. It cannot be assumed that similar results would be obtained if the same concentration of DDT as that dusted over the pasture was applied as a spray.

(i) *Repellency effect of DDT*

There was no visual evidence of repellency the day after DDT was applied. However, bee counts showed repellency from the time of application on 11th until 14th December, when there was no bee flight. Heavy rain on the 15th evidently washed off the bulk of the DDT as there was no further evidence of repellency. Light rain (6 points) which fell on the day the DDT was applied was not considered to have washed off any appreciable quantity. The rain, by causing the DDT to adhere to the clover flowers, would probably result in it remaining on longer than if it were exposed in a dry state to the frequent local winds. Repellency was also observed in an area of 1 ac. dusted with DDT.

The decrease of DDT residues on clover flowers is shown to be closely related to prevailing weather conditions. Analytical results taken in conjunction with bee mortality and field observations on repellency indicate that there is a relationship between insecticide concentration and repellency.

The DDT was strongly repellent to bees during the period when toxicity was highest. This property would considerably reduce mortality in dusted areas by lowering the density of bees.

It is not advisable to draw too close a comparison between the results obtained when white clover pasture is dusted with DDT plus superphosphate and those following the application of DDT to other types of plant. The methods used by bees in collecting nectar from different kinds of flowers vary and must have some effect on their exposure to DDT dusts. Methods of applying dusts, and climatic conditions following dusting, are also liable to affect results. Many workers do not state the p.p.i. content of the DDT used in experiments. Materials mixed with the DDT dusts may also affect the action of the DDT on bees.

Several workers have concluded that DDT dusts repel bees. Linsley and MacSwain⁴ studied the effect on bees of dusting alfalfa in bloom with DDT. Following dusting they noted a depression of bee population which they thought might be caused by repellency. Smith *et al.*⁵ observed the effect on bees of dusting an alfalfa field in bloom with 30 lb. of 5% DDT per acre, i.e. 1.5 lb. of DDT per acre. They noted a very definite depression of the field population of bees in the dusted area compared with prior activity. The authors considered this was due to the DDT exerting repellency. Repellency was not observed directly as in the present investigation. Ghani and Shaw⁶ studied the repellency of DDT applied as a 5% dust to dandelion flowers. They found that repellency did occur.

(ii) *Effect of DDT on bee mortality*

The general opinion of workers is that dusting pasture in bloom with DDT does not affect apiaries severely. Linsley and MacSwain⁴ considered that large scale bee mortality under field conditions had not yet been demonstrated. McGregor and Vorhies³ concluded that dusting cotton fields with 10% DDT in pyrophyllite at 15 lb. per acre, or with 5% DDT in sulphur at 20 lb. per acre, or spraying with 1.5-3 lb. of DDT dissolved in xylene per acre, are not a danger to commercial beekeeping. Smith *et al.*⁵ found that the effect on colonies was still small even after three dustings. Way and Synge¹⁵ concluded that commercial applications of DDT are harmless to bees. Ghani and Shaw⁶ found that DDT showed a fairly high level of toxicity but their experiment was not based on commercial application.

The DDT plus superphosphate and the superphosphate were both applied early in the morning before bees had commenced visiting the pasture. Thus, bees were not dusted directly. When caged bees were heavily dusted with superphosphate, no mortality occurred, but similar dusting with DDT plus superphosphate, caused 100% mortality within 24 hr. Although these bees were more heavily dusted than they would be in practice, mortality would be expected if field bees were present on pastures during dusting. However, the movement of the trucks operating the spreaders would frighten off many bees from the pasture before dust could reach them and the strong repellency of the DDT would drive off still more. Therefore, such losses of bees are not considered likely to be of importance.

As clover pastures have been extended and improved, grass grub damage has shown a parallel increase. The magnitude of the loss from this cause may be realised when it is stated that in 1939 it was estimated that 30,000 of 80,000 acres damaged in Canterbury would have to be resown¹. Damage to clover pasture would result in reduced honey crops. The effective method of grass grub control now being applied should increase honey crops in many areas.

BHC is considered by all workers to be much more toxic to honey bees than DDT. Hocking¹⁶ in his estimated danger index allots a figure of 0.02 for DDT and 5.0 for BHC. Therefore the application of BHC for grass grub control must be regarded as potentially highly dangerous to bees until its effect can be fully investigated.

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